CONTROLLED POLYMER ADSORPTION FOR ENHANCED SELECTIVITY IN FLOCCULATION

By

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To my parents, Kiran and Sushil Behl
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Abstract of Dissertation Presented to the Graduate School of
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CONTROLLED POLYMER ADSORPTION FOR ENHANCED SELECTIVITY IN FLOCCULATION

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Flocculation of fine particles is critical to solid-liquid and solid-solid separation technologies. Selective flocculation involves selective aggregation of a desired particulate constituent from a dispersed mixture using a high molecular weight polymer, followed by separation of the flocs by either sedimentation or floc flotation. Selection of the flocculant is based on single component tests. Often the selectivity observed with single components is not realized with mixtures. The loss in selectivity has been attributed to heterocoagulation, dissolved ion activation, entrainment and entrapment. Recently heteroflocculation has been proposed to be another major factor in the loss of selectivity. It has been argued that the polymer adsorbed on the inert component bridges with the active (flocculating) particles to form floc, leading to heteroflocculation.

According to a recently developed mathematical model, heteroflocculation can be minimized either by employing a highly selective flocculant, or by using extremely small dosages of the polymer. These approaches, however, are not practical in most cases. In the present study another method to reduce heteroflocculation has been proposed. This involves poisoning or blocking the "active sites" on the inert component by a site blocking agent (SBA).

In this study the use of lower molecular weight fraction of the flocculant itself (poly ethylene oxide) as an effective site blocking agent in a dolomite-apatite system is discussed. It has been demonstrated both experimentally and mathematically that the lower molecular weight fraction of a flocculant, which is incapable of flocculating the particles, is an efficient site blocking agent. The most effective SBA was determined to be the highest molecular weight fraction of the flocculant itself which was not capable of flocculating any of the components of the mixture. In the presence of the SBA, flocculant adsorption decreased significantly on apatite particles thereby inhibiting their co-flocculation. This lead to a near complete separation of apatite from dolomite.

Adsorption, FT-IR, zeta potential and heat of adsorption measurements were performed to understand the interaction of the flocculant/SBA with apatite and dolomite surfaces. It was determined that only dolomite with isolated hydroxyl groups exhibited flocculation.

CHAPTER 1
INTRODUCTION

Selective Flocculation Process

Solid-solid separation is an important unit operation for recovering values from a mixture. The limited performance of the conventional physical separation methods such as sedimentation, electrostatic and magnetic separations for treating fine particles [Som79, Som80, Att82, Mou85] has necessitated the development of alternative technologies for processing fine particles. It should be noted that the term "fines" has no rigid defined size range but typically it is taken as sizes below 50 microns, where the bulk properties no longer govern the particle behavior in suspensions. In this range, the surface chemical forces become dominant and can be applied to achieve the desired separation. Among the many new techniques proposed for fine particle separation, selective flocculation has shown considerable promise [Yar70, Rub75, Rea76, Att78, Sre78, Col79, Drz81, Att82, Yar82, Att87b, Yu87, Att88a]. This process involves flocculating particles of one type, from a well dispersed suspension of the ore or a mixture, followed by separation of the flocs by either floc flotation or sedimentation. Selective flocculation, like flotation (typically used for coarser particles, of the order of 100 microns), takes advantage of the differences in the physico-chemical properties of the particles but, unlike flotation, does not depend entirely on the wettability characteristics of the particle surfaces.

The major application of selective flocculation has been in mineral processing, but many potential uses exists in the biological and other colloidal systems [Yu87]. These include purification of ceramic powders, separating hazardous solids from chemical waste and removal of deleterious components from the paper pulp [Lin83]. Industrial applicability of this process has been limited to a few cases, such as processing of taconite and potash ores, because results obtained for selectively flocculating natural ores or complex synthetic mixtures often do not correlate with the observed selectivity in single component tests. A number of reasons such as heterocoagulation, charge patch neutralization, dissolved ion activation, entrapment and entrainment have been suggested for the observed loss in selectivity [Rub75, Sad80, Bag85a, Bag85b, Kri85, Sla85, Att87b, Att88, Aca89, Att89, Pra91a, Pra91b]. Efficient mechanical and chemical design of the process, to a large extent, could overcome the loss in selectivity due the above mentioned reasons. For example, heterocoagulation takes place because of agglomeration of particles with unlike charges, which can be minimized by properly dispersing the ore.

Selective flocculation may be defined as a three-step process: (1) dispersing the fine particles, (2) selectively adsorbing the polymer on the active component (flocculating particles) and forming flocs, and (3) separation of the flocs. Among the three steps, the second step, i.e., selective adsorption of the flocculant, is the most difficult to control and is by far the limiting step to the success of the selective flocculation process [Att87a, Mou91].

Selective Adsorption Of The Polymers

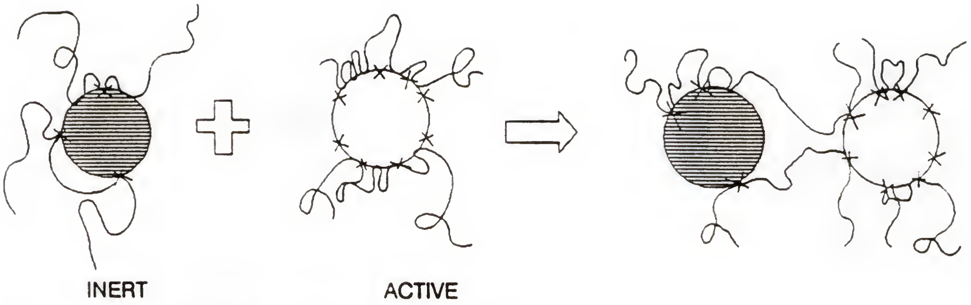
Selective flocculation of a particular solid from a mixture cannot be achieved unless the polymeric flocculant selectively adsorbs only on one component. Therefore, the ability of the polymer's functional groups to exploit the differences in the surface chemical behaviors of the various particles to yield selective adsorption is one of the major parameters. In order to select a polymer for selective adsorption, three main interactive factors namely, (1) the flocculant, (2) the surface, and (3) the suspending medium must be considered. Selective adsorption of the polymer on a particular surface is the result of the interactions between the functional groups and the binding sites on the surface. Clearly the surface property chosen (hydrophobicity, hydroxyl groups, surface charge or chemical bonding) as the basis for selective adsorption must represent the one with the greatest difference between the flocculating and non-flocculating particles. The larger is the difference, the better is the selectivity in adsorption. However, it should be noted that flocculants are high molecular weight polymers, therefore, it is difficult to selectively adsorb the flocculant on solid surfaces since macromolecules are known to adsorb through mechanisms such as hydrogen bonding, hydrophobic interactions, electrostatic interactions, chemical bonding or van der waal forces. According to Moudgil and co-workers [Mou87b, Mou87c, Mou87d, Mou89b, Mou91], the nonselective adsorption of the flocculant would make it possible for the inert component to co-flocculate with the active component thereby exhibiting loss in selectivity .

The aim of this study was to understand the parameters that control selective adsorption of the polymer (flocculant), thereby achieving the desired separation in a model system comprising of a mixture of apatite and dolomite with polyethylene oxide as the flocculant.

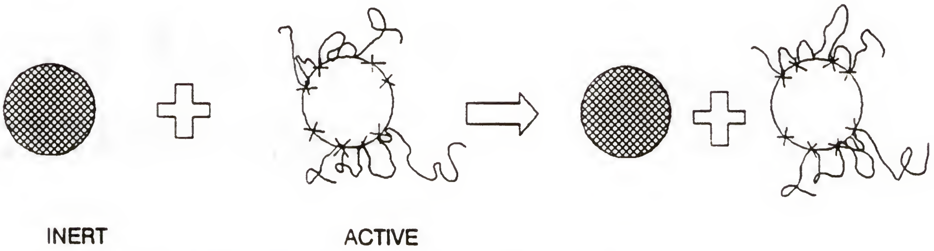
CHAPTER 2
BACKGROUND

Introduction

Separation of dolomite from apatite using selective flocculation technique was attempted by Moudgil et al. [Mou87b, Mou87c, Mou87d, Mou89b, Mou91] and Shah [Sha86]. The flocculant used was polyethylene oxide of 5 million molecular weight. Single mineral tests indicated that poly(ethylene oxide) flocculated dolomite and not apatite. However, mixed mineral tests did not exhibit the expected selectivity. The previously documented reasons for the loss in selectivity like heterocoagulation, dissolved ion interference, mechanical entrapment in the flocs and inertial entrainment of the inert material between the floc, had minimal effect in this system. "Polymer induced entrapment" or heteroflocculation was determined to be the major cause for the observed loss in selectivity [Mou87b, Mou87c, Mou87d, Mou89b, Pra91a]. These investigators argued, assuming bridging to be the flocculation mechanism, that the polymer adsorbed on the inert component bridges with the active (flocculating) particles to form a floc, leading to heteroflocculation. A schematic representation of this phenomena is given in Figure 2.1. Higher adsorption of the flocculant on the active component (dolomite in this case) was explained on the basis of availability of larger number of "active sites" on the surface. The active site concept as proposed by Moudgil and coworkers [Mou87c, Mou91] is slightly different from the binding site concept proposed earlier [Sch79, Sch80, Lyk85]. A binding site is defined as the actual site where an adsorption bond is formed



(i) Some "active" sites on the inert constituent: No selectivity



(ii) No "active" sites on the inert substrate: Selectivity achieved

x = active sites, ~ = polymer molecule

Figure 2.1: Schematic For Heteroflocculation.

between the solid surface and the binding monomeric unit of the polymer: the active site on the other hand, is the area occupied by the adsorption of one molecule of the polymer. A semiqualitative model was proposed by Moudgil et al. [Mou87c], using the active site concept, to describe the efficiency of collisions in flocculation. Based on this theory, a mathematical model, outlined below, was proposed by Moudgil and Behl [Mou91] to identify the conditions for selective flocculation.

Mathematical Model

Polymer adsorption on the solid is assumed to be irreversible, as is the case for adsorption of polymers and macromolecules on solid surfaces [Sin73]. This assumption is valid for the time scale involved (of the order of few minutes) in the selective flocculation processes. It was inferred by Wagberg [Wag87] that polymer adsorption on powders is rapid, since almost instantaneous flocculation is observed with high molecular weight polymers. Also, it was suggested that turbulence markedly increases the rate of polymer adsorption by aiding in collision of the polymer molecules with the particles. If the adsorption of the polymer is assumed to be a result of polymer (molecule) - particle collisions, the rate of adsorption would be at least a magnitude higher than the rate of particle-particle collisions. For example, at a typical dosage of 0.1 mg of the polymer per gram of the solid (i.e., about 10^{14} polymer molecules per 10^{8} particles), the number of polymer molecules is 10^{3} - 10^{7} times greater than the number of particles. It can, therefore, be assumed that the polymer adsorption is extremely fast and the particle-particle collisions is the rate controlling step. It is assumed that the particles are liberated and large enough to neglect the Brownian diffusivity. The loss in selectivity due to other possible mechanisms such as heterocoagulation, entrapment, entrainment, etc., is also assumed to be minimal.

The model considers only the binary collisions between the particles/clusters in a manner consistent with well known orthokinetic flocculation suggested by Smoluchowski [Smo17]. The rate expression for selective flocculation is slightly modified form of Smoluchowski's expression and is given by

$$F_{ij} = K\, n_i\, n_j\, E_{ij} \tag{2.1}$$

where

F_{ij} = rate of aggregation of species i with j

K = flocculation rate constant

n_i , n_j = number of interacting species per unit volume

E_{ij} = collision efficiency factor (expanded later in this chapter)

The rate of flocculation K according to Smoluchowski's interpretation of orthokinetic flocculation is given by the following expression

$$K = \frac{k'}{6}\, \bar{s}\, (d_i + d_j)^3 \tag{2.2}$$

where

k' = constant, depends on hydrodynamic and electrostatic parameters

$\bar{s}$ = mean velocity gradient

d_i , d_j = particle diameters

A number of expressions for the collision efficiency have been suggested in the literature by Smellie and LaMer [Sme57], Hogg [Hog84], and Moudgil et al. [Mou89b]. The expression by Moudgil et al. and Hogg accounts for heteroflocculation, while the other was developed for bulk flocculation. In fact, in the limiting case, Moudgil's expression given below [Mou87c; Mou89b] reduces to the corrected version of the one suggested earlier by Smellie and LaMer [Sme57].

$$E_{ij} = \Phi_j^2 \, \Phi_R \, [\theta_i(1-\theta_j) + \theta_j(1-\theta_i)] \tag{2.3}$$

where

Φ_i, Φ_j = fraction of sites on i and j that are active for polymer adsorption

θ_i , θ_j = fractional surface coverage (of active sites) at a given polymer dosage

Φ_R = ratio of "active sites" on the active component to "active sites" on the inert component = $(\frac{\Phi_i}{\Phi_j})$; $\Phi_R > 1$ (by definition),

Since the floc growth is accompanied by reduction in the specific surface area and mobility of the flocs, the constant k′ is modified as

$$k' = k'' \frac{1}{\rho_i^{\frac{1}{2}} d_i^{\frac{3}{2}}} \frac{1}{\rho_j^{\frac{1}{2}} d_j^{\frac{3}{2}}} \tag{2.4}$$

where

ρ_i and ρ_j = densities of the species i and j

k′′ = rate constant

Accordingly, the rate equation is modified as

$$F_F = K'_{F_{ij}} \left(\frac{n'_{F_{ij}} \, \overline{n}_{F_{ij}} \, [d'_{F_{ij}} + \overline{d}_{F_{ij}}]^3}{\rho'^{\frac{1}{2}}_{F_{ij}} \, \overline{\rho}^{\frac{1}{2}}_{F_{ij}} \, d'^{\frac{3}{2}}_{F_{ij}} \, \overline{d}^{\frac{3}{2}}_{F_{ij}}} \right) E_{ij} \tag{2.5}$$

where

F_F = rate of agglomeration of interacting flocs consisting of two types of flocs (or particles) i and j.

$K'_{F_{ij}}$ = flocculation rate constant: depends on the system, hydrodynamics and electrostatic parameters

$n'_{F_{ij}}$ and $n_{F_{ij}}$ = number of flocs of diameter $d'_{F_{ij}}$ and $d_{F_{ij}}$ respectively per unit volume.

$\rho'_{F_{ij}}$ and $\rho_{F_{ij}}$ = density of interacting flocs.

Equation 2.5 can be rewritten for any interaction (floc-floc/particle, etc.) as

$$F_F = k\, n_i\, n_j\, E_{ij} \tag{2.6}$$

where

k is a constant in which all the other parameters of equation (2.5) are lumped.

Applying the model to a single mineral, which is active for polymer adsorption (i.e., high E_{ij} ~0.1 - 1.0), the above equation will yield high flocculation rates indicating appreciable floc formation, as expected. In case of flocculation of inactive/inert particles, E_{ij} is low, typically 10^{-6} to 10^{-3}; however, for an extremely large number of particles, a reasonable amount of flocculation would be predicted since the rate has a square dependence on n (number) as compared to a linear dependence on E_{ij}. This, however, is not observed experimentally [Sha86, Mou87c]. To further understand this, E_{ij} has to be considered in some detail. The model prediction of selectivity achievable during the flocculation of two dissimilar surfaces is based on the active site ratio. In single mineral flocculation this can be misleading as the actual number of sites on the inert material may be very small, and since only those collisions where particles collide with the right orientation, i.e., collision of polymer coated active site with a bare active site or vice versa, are considered to lead to floc formation, the number of flocs formed will be small. In other words, no appreciable flocculation would occur. In this case estimating the actual number of active sites may be more useful, which off-hand seems to be difficult. To take this into account in the model for computational purposes, a parameter called "critical collision efficiency" is introduced. In case the collision efficiency parameter is below the critical value, an extremely large number of collisions are required for an appreciable floc formation and in the model, floc formation is assumed to be absent. However, a value below critical E_{ij} does not mean that there is no floc formation; it implies that it is not significant and, therefore, the rate is negligible. The value of critical E_{ij} would be system specific and is determined experimentally.

The particle-particle collision in orthokinetic flocculation is induced by hydrodynamic shear, and not by Brownian motion. This shear will lead to hydrodynamic stress, which the floc may not be able to withstand, leading to floc breakage [Gre76, Gre82]. Two main mechanisms of floc breakage, namely splitting and erosion, are suggested in the literature [Gla82, Pan82, Ray87]. If floc formation is induced by high molecular weight polymeric flocculant, resistance to breakage is high since the binding strength of these flocs is high [Ray87, Mou89a]. Unlike coagulation, floc breakage in case of polymer induced flocculation has shown to be irreversible [Ray87, Mou89a].

Many formulations have been suggested in the literature to model floc breakage. These are broadly classified in two categories

1. breakage due to hydrodynamic stresses/conditions [Tho66, Fir76, Smi78, Muh87] and
2. by viewing it to be a stochastic process [Gla82, Pan82, Ray87]

Ray and Hogg [Ray87] have recently based floc breakage phenomena on mass-size population balance to model the breakage function by drawing a parallel with the comminution process. Assuming floc-floc interaction to be absent for the breaking, they concluded that it is a first order process. Also, they suggested that reagglomeration is almost absent until fresh polymer is added, a conclusion observed also by Moudgil et al. [Mou89a].

In any case, if there is a floc breakage due to splitting, the daughter flocs may be expected to be identical to the parent floc. The heterofloc is expected to break randomly since floc formation is a random process, unless there are some preferential splitting paths for which, a priori, there is no reason. Also the effect due to erosion of flocs would be negligible for estimating selectivity, since it has been suggested that erosion takes place in flocs greater than some minimum size [Muh87, Tsa89], which increases as the shear rate decreases. Therefore, effect of erosion is small until a very large shear rate is applied.

In view of the above argument, the breakage of the flocs has been neglected to model selectivity during floc formation. However, to study recovery, this assumption may be erroneous.

The above equations are used to determine floc formation for a given system using a computational scheme, which is described next.

Computational Scheme

The computational scheme is outlined in Figure 2.2. It involves a step-wise evaluation of maximum number of flocs of a particular type that are possible. Then the rate of the particular type of floc formation is estimated by assuming that all the types of collisions are independent of each other, and therefore the probability for this to occur would be the fraction of the total rate. Once floc formation takes place, floc size (d_{floc}) is estimated using Vold's [Vol63] equation, and for ρ_{floc} this equation is slightly modified by dividing the net mass of solids and entrapped water in a spherical volume of diameter d_{floc}. The θ and Φ for a floc are calculated as the surface area weighted average of the

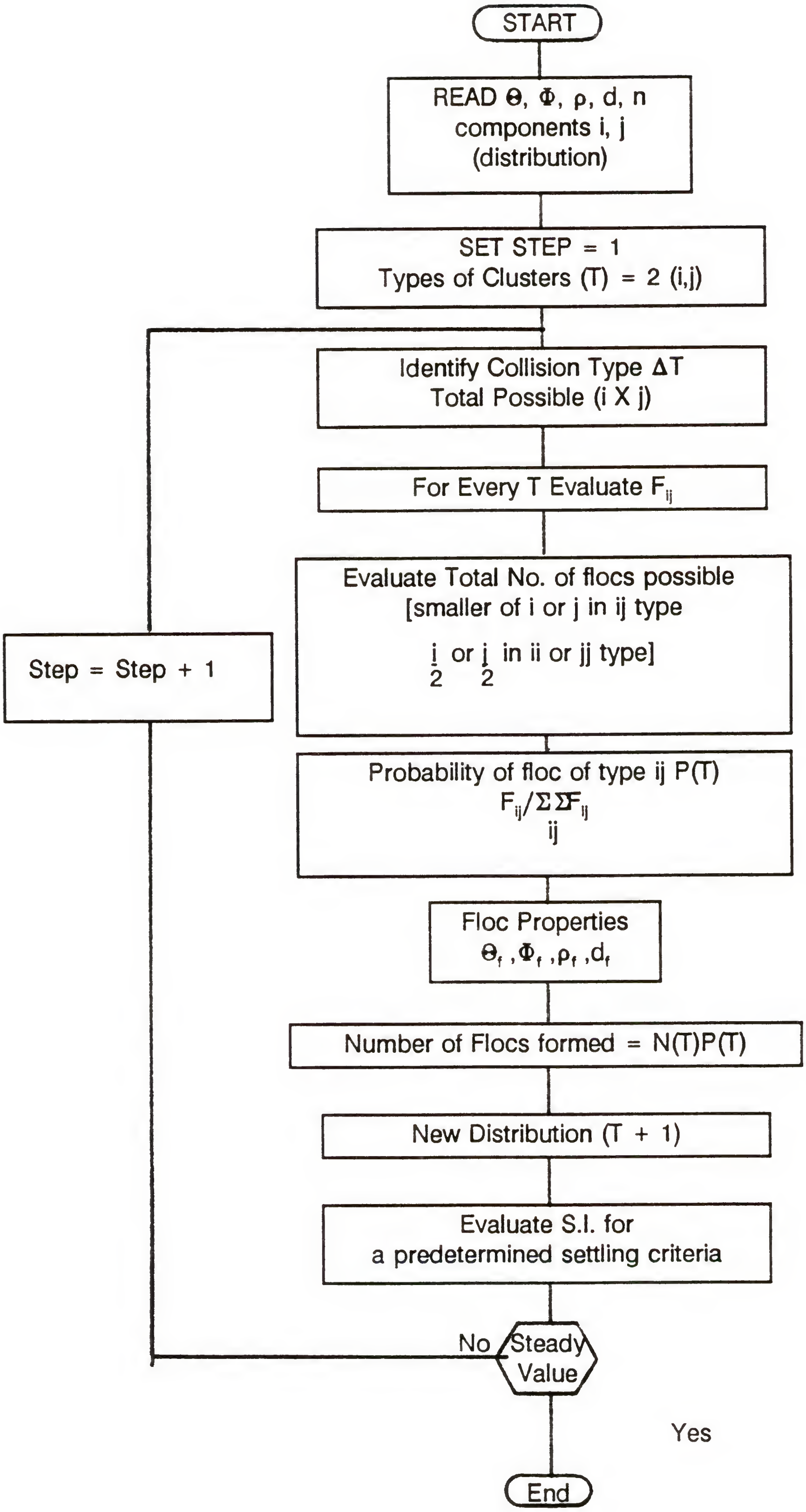

START
READ Θ, Φ, ρ, d, n
components i, j
(distribution)
SET STEP = 1
Types of Clusters (T) = 2 (i,j)
Identify Collision Type ΔT
Total Possible (i X j)
For Every T Evaluate F_{ij}
Evaluate Total No. of flocs possible
[smaller of i or j in ij type
$\frac{i}{2}$ or $\frac{j}{2}$ in ii or jj type]
Probability of floc of type ij P(T)
$F_{ij}/\sum_{ij}\sum F_{ij}$
Floc Properties
$\Theta_f, \Phi_f, \rho_f, d_f$
Number of Flocs formed = N(T)P(T)
New Distribution (T + 1)
Evaluate S.I. for
a predetermined settling criteria
Steady Value
No
Yes
Step = Step + 1
End

Figure 2.2: Schematic Of The Computational Scheme. [Mou91]

individual particles constituting a floc. The value of θ and Φ for a pure floc (i.e., floc of same material) is the same as that of a single particle since the exposed surface still has the same characteristics. Flocs satisfying a predetermined separation criteria are assumed to be separated from the bulk. At each step, the selectivity index (S.I.) is calculated; simulation is stopped once a steady value is reached. The term selective index is a measure of selective floc formation and is given by the following expression

$$\text{Selectivity Index (S.I)} = \frac{\%G_c - \%V_f}{100 - \%V_f} \text{ X } 100 \tag{2.7}$$

where

$\%V_f$ = % value in the feed

$\%G_c$ = %grade in the concentrate; where %grade is defined as

$$\%grade = \frac{V_c}{T_c} \text{ X } 100 \tag{2.8}$$

V_c and T_c are the amount of values in the concentrate and the total amount of concentrate. In a few cases, where the number of particles were extremely large, due to limited computational storage, the process was carried out to as far as possible and the results extrapolated.

Comparison With Experimental Results

A number of experimental results for different systems described in earlier work (Mou91) were obtained and compared with the predicted values. A typical comparison is shown in Figure 2.3. A good agreement between the experimental and predictive results is obtained. Most simulations involved 40 to 60 steps, and the computational time for the simulation on VAX 11-780 was less than 10 CPU Minutes.

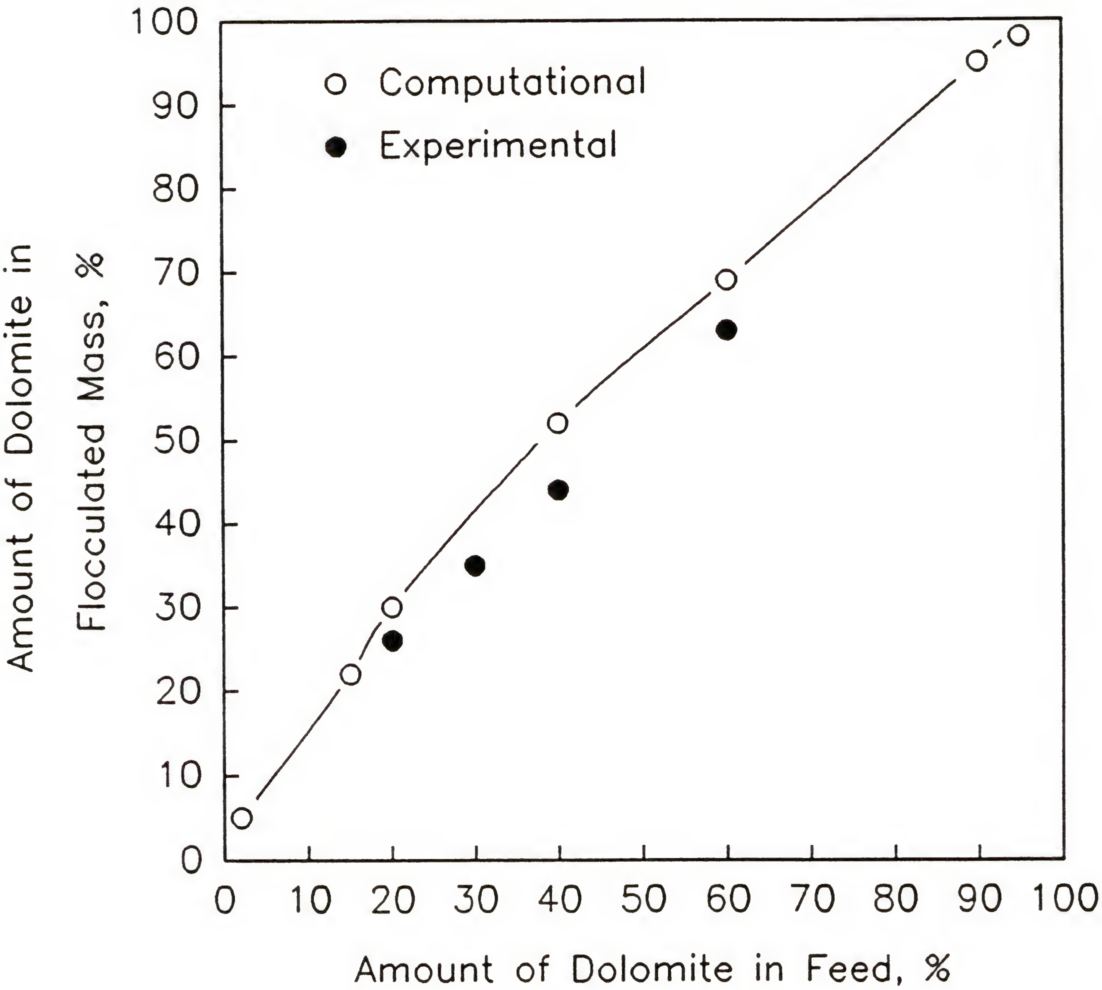


Figure 2.3: Comparison Of Computational And Experimental Data For Selective Flocculation.

Since the model had predictive capabilities, it was used to identify optimum conditions, e.g., polymer dosage for separation in a given mineral system. It can be seen from Figure 2.4 that a high Φ_R value would give excellent selectivity in floc formation. This, however, may not be easily achievable, since flocculants are typically of high molecular weight and adsorb on the solid surface due to a number of mechanisms such as hydrogen bonding, hydrophobic interaction, electrostatic interaction and covalent bonding [Att87a]. The other alternative for a low Φ_R value, a high selectivity in floc formation, may be obtained by properly adjusting polymer dosage to attain low θ_{inert}. This, however, could effect the floc properties thereby making floc separation inefficient. Clearly, the two strategies as suggested by the model may not always be practical.

An alternate strategy is suggested in this work to achieve selective floc formation by either poisoning or blocking the active sites on the inert component. Molecules used to block the sites should not be capable of flocculation themselves and are termed as Site Blocking Agents (SBA) [Beh92]. SBA action is schematically is shown Figure 2.5. It can be observed that if the SBA molecules are capable of blocking the same sites where the flocculant adsorbs, then it should be possible to achieve a high Φ_R value as well as low θ_{inert}. These are the two conditions predicted by the model for selective floc formation by controlling heteroflocculation.

Scope Of The Present Study

The specific objectives of this investigation are as follows:

1. Understanding the mechanism of selectivity in mixed mineral flocculation

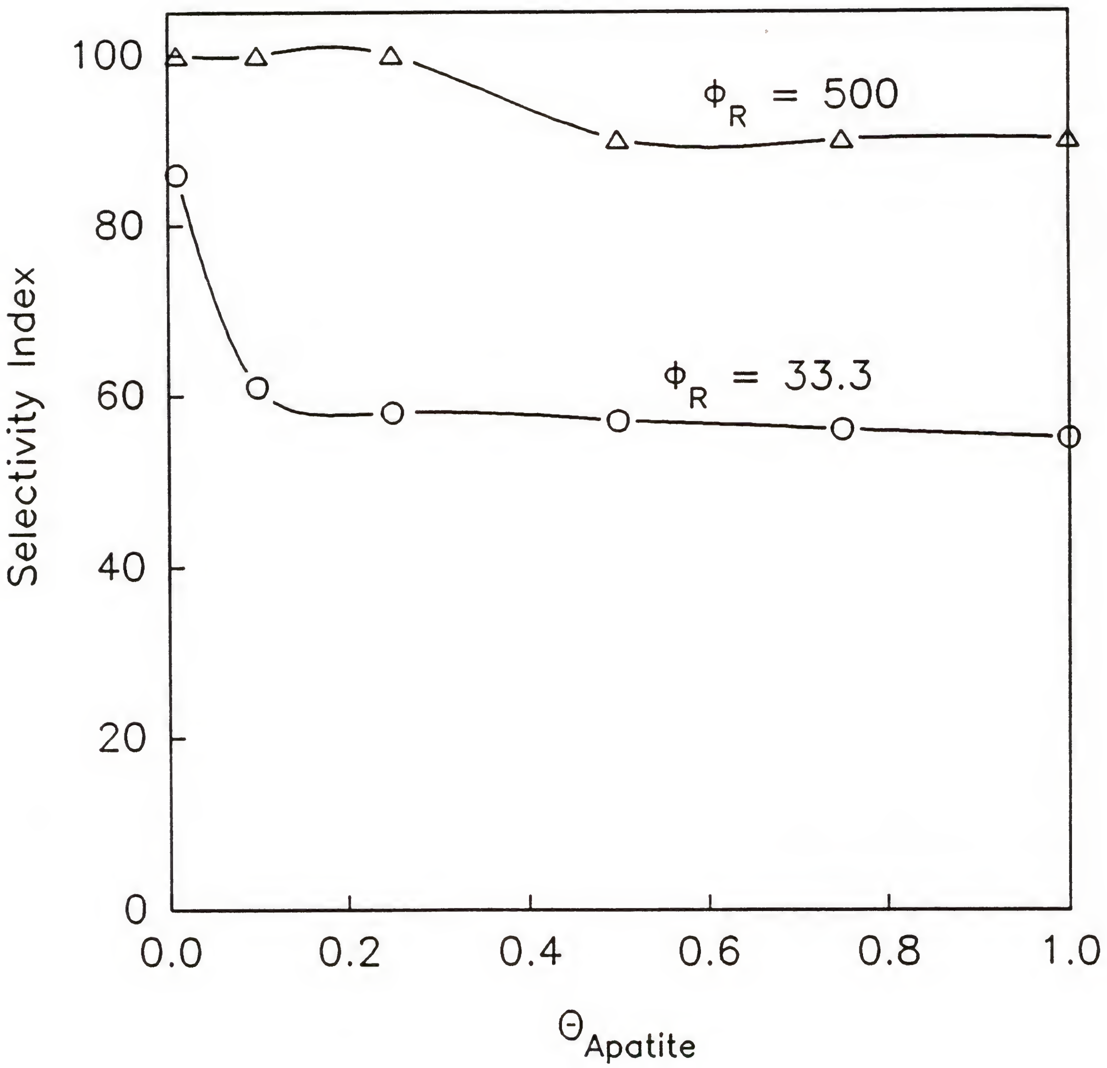


Figure 2.4: Effect Of θ_{inert} On Selectivity Index.

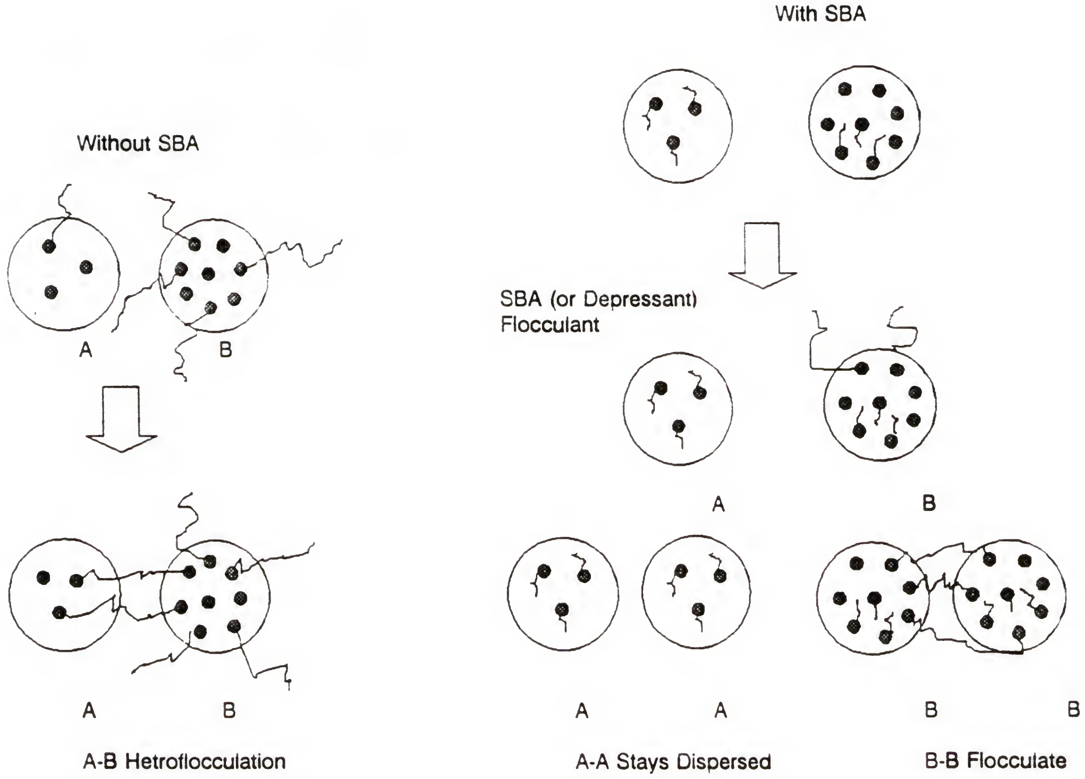


Figure 2.5: Schematic Showing Site Blocking Agent (SBA) For Enhanced Adsorption of the Flocculant.

2. Understanding the mechanism for adsorption of poly(ethylene oxide) on apatite and dolomite surfaces
3. Enhanced selective adsorption of the flocculant on the flocculating component
4. Exploring the possibility of using lower molecular weight fraction of the flocculant itself as site blocking agents (SBA).
5. Separation of apatite from dolomite by selective flocculation technique.

CHAPTER 3
EXPERIMENTAL

Materials

Dolomite

The dolomite samples used in this study are listed in Table 3.1. As-received samples, after desliming and drying at 140 °C, were crushed using a Chipmunk crusher and pulverized. The pulverized material was dry ground in a high purity ball mill to obtain -400 mesh fraction (less than 38 µm). The samples were stored in glass jars and used as required.

Apatite

A sample of high grade phosphate rock (fluorapatite) was supplied by Agrico. Chemical Company, Florida. This sample was prepared using the same procedure as for dolomite described above.

Polymers

Poly(ethylene oxide) (PEO), a water soluble partially hydrophobic polymer, was used in this study. The characteristics of the various polymers used and their sources are given in Table 3.2. These samples were used as received.

Table 3.1: Source Of Dolomite Samples.

MINERAL	SOURCE	LOCATION	LABEL
Dolomite (K-36)	Agrico Chemical Co.	Central Florida	Sample "A"
Dolomite (Yellow)	Agrico Chemical co.	Central Florida	Sample "B"
Dolomite (Rock)	IMC Fertilizer, Inc.	Central Florida	Sample "C"
Dolomite (4 Corners)	IMC Fertilizer, Inc.	Central Florida	Sample "D"
Dolomite (Crystalline)	Ward's Natural Science Establishment, Inc.	New Jersey	Sample "E"
Dolomite (Perry)	Perry Mines	South Georgia	Sample "F"

Table 3.2: Characteristics Of The Polymers Used In This Study.

Name[x]	Molecular Weight	Source	Radius of Gyration, R_g (Å)*
PEO	5×10^6	Polysciences, Inc.	1440
PEO	1×10^5	"	1263
PEO	6×10^5	Aldrich, Co.	521
PEO	6×10^5	Polysciences, Inc.	409
PEO	1×10^5	"	409
PEO	1.85×10^4	"	56
PEG	3.40×10^3	"	32

* Calculated according to expression by Bailey and Koleske [Bai76]

x PEO: Poly(ethylene oxide); PEG: Poly(ethylene glycol)

Other Chemicals

All experiments were conducted in deionized water (DI) with conductivity less than 100 micromhos/cm. Dilute nitric acid (HNO_3) and potassium hydroxide (KOH) were used as pH modifiers. Sodium silicate obtained from Fischer Scientific Co. was used as a dispersant.

Methods

Mineral Characterization

The mineral samples used in the study were characterized by the following methods

Chemical analysis

Bulk chemical analysis of the samples was performed using a Perkin Elmer II, inductively coupled plasma (ICP) emission spectrometer. The P_2O_5, MgO and acid insoluble contents of the various samples are presented in Table 3.3. These samples are chemically similar to those used in some of the earlier work [Cha86, Sha86, Inc87]. Trace impurities of Al^{3+}, Fe^{3+} and organic matter were detected in both apatite and dolomite.

Table 3.3: Chemical Analysis of the Samples.

Mineral	P_2O_5, %	MgO, %	Acid Insol.,%
Dolomite A	0.93 ± 0.3	19.10 ± 0.4	2.02 ± 0.4
Dolomite B	2.86 ± 0.4	15.53 ± 0.6	2.78 ± 0.6
Dolomite C	2.26 ± 0.5	16.13 ± 0.3	5.30 ± 0.4
Dolomite D	1.70 ± 0.4	17.25 ± 0.5	6.11 ± 0.6
Dolomite E	-	21.10 ± 0.3	-
Dolomite E	-	18.77 ± 0.2	-
Apatite	34.88 ± 0.7	0.25 ± 0.1	2.05 ± 0.5

X-ray analysis

X-ray diffraction analysis was performed using APD3720, Cu-Kα (Philips Electronics) diffractometer, of apatite and dolomite samples are presented in Figures 3.1-3.4. Minor peaks of quartz and other impurities are seen in some of the samples. For example, in the X-ray pattern of apatite some dolomitic impurity is observed and vice versa. The major peaks (Figure 3.2-3.4) in all the dolomite samples (B to F) correspond to dolomite structures.

Mineral dissolution studies

These tests provide the information about the dissolution characteristics of the various species from the mineral surface. This information is helpful in explaining adsorption behavior and determining conditions for adsorption with minimal ionic interference. Analysis of the dissolved ions such as calcium, phosphorous and magnesium was performed using a Perkin Elmer II, inductively coupled plasma (ICP) emission spectrometer.

Particle Characterization

The mineral particles were characterized according to their size, surface area and porosity. The morphology of the particles was examined using a scanning electron microscope (SEM).

Particle size

The particle size distribution of the samples was measured using micromertics X-ray Sedigraph 5100 particle size analyzer. The mean particle size of the samples varied from 4 to 11 µm (see Table 3.4). Further the particles exhibit a broad size distribution (see Figure 3.5).

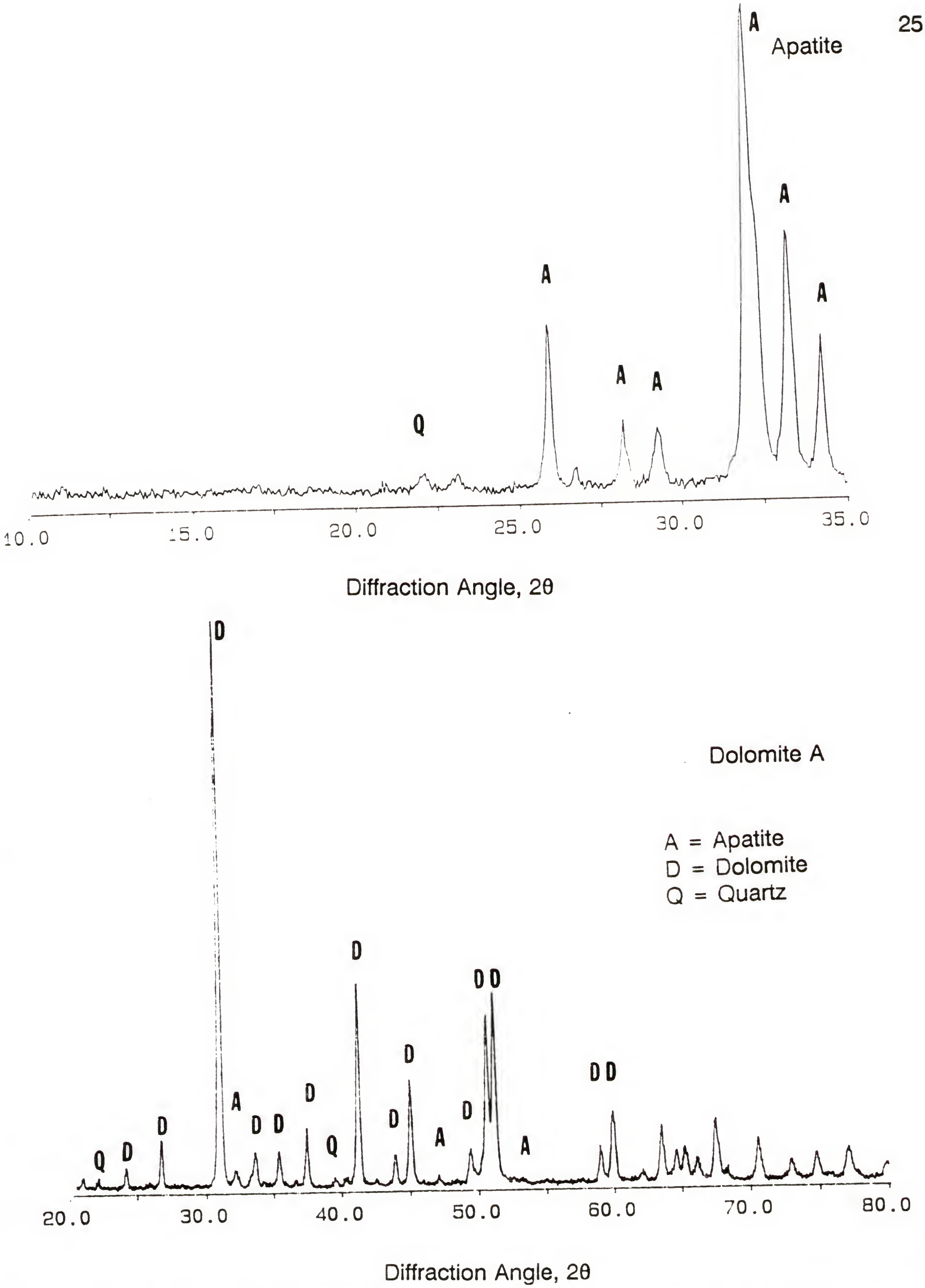


Figure 3.1: X-ray Diffraction Pattern For Apatite and Dolomite (A) Samples.

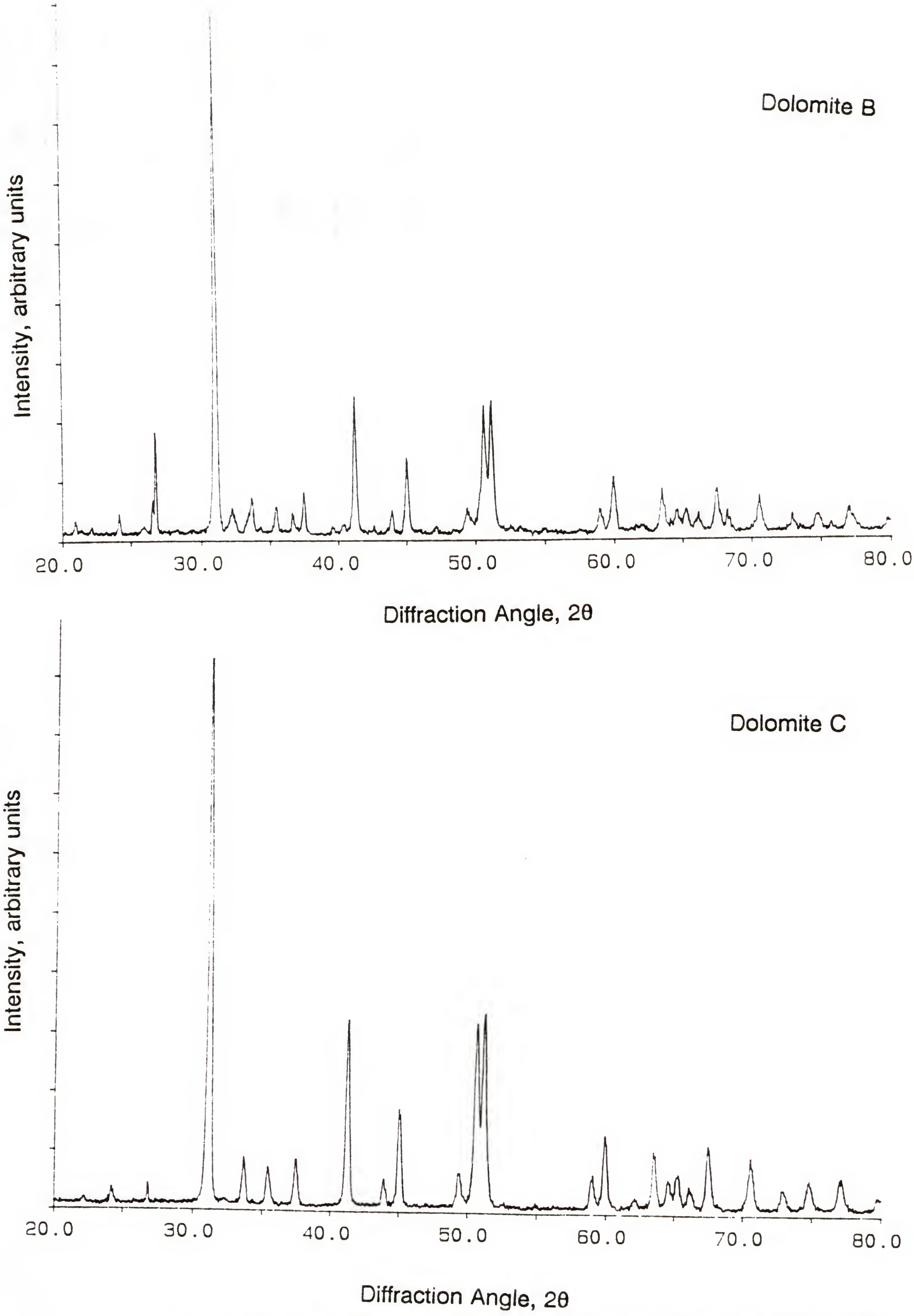


Figure 3.2: X-ray Diffraction Pattern For Dolomite Samples (B and C).

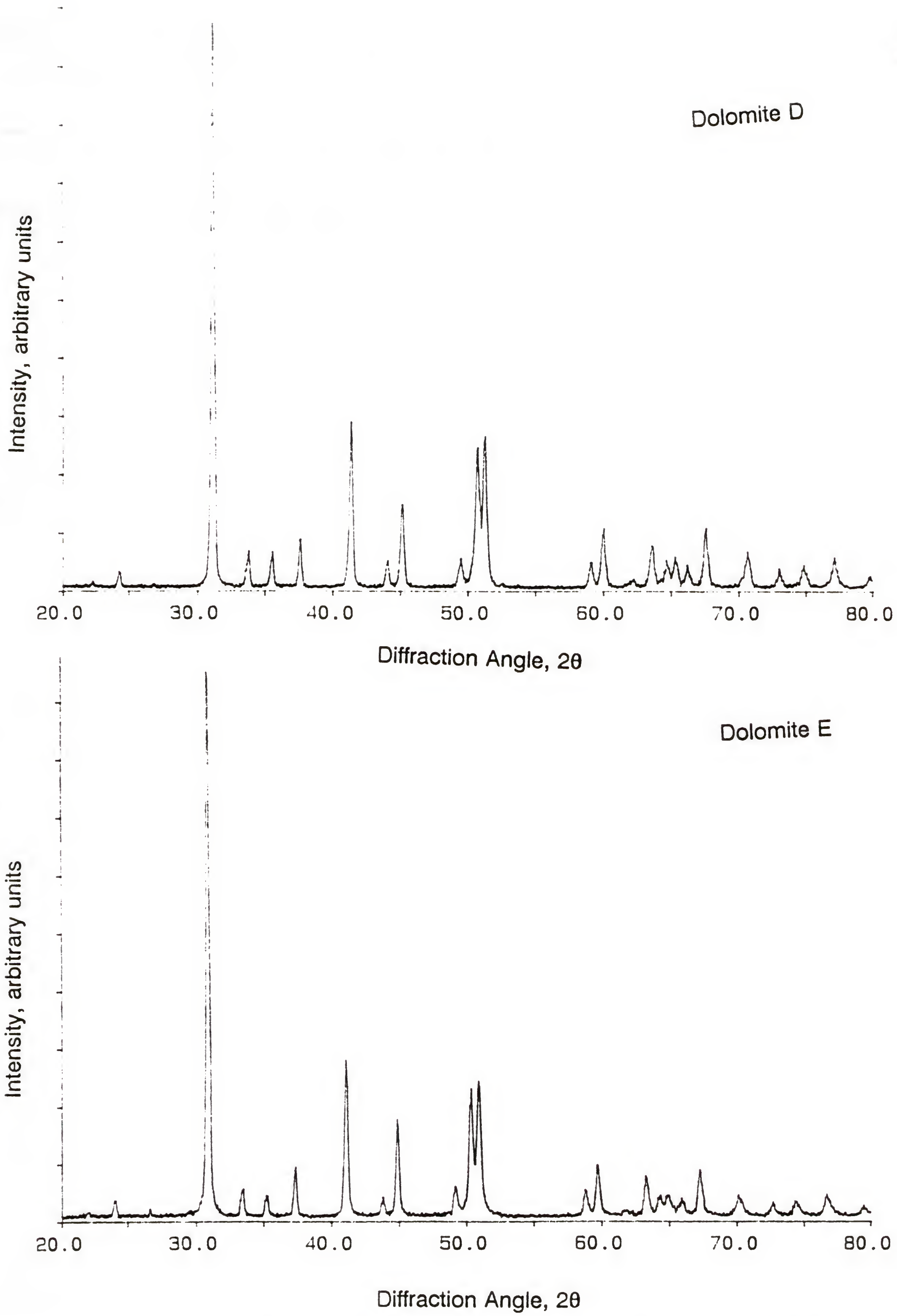


Figure 3.3: X-ray Diffraction Pattern For Dolomite Samples (D and E).

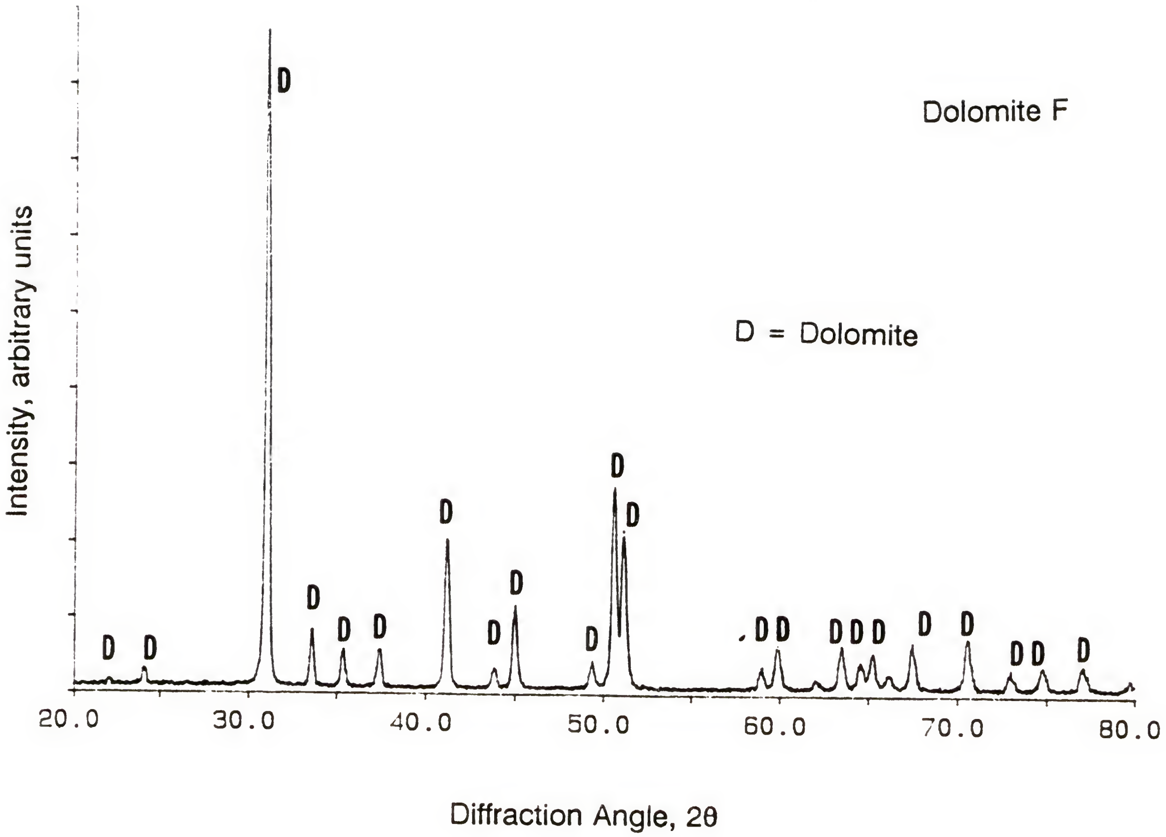


Figure 3.4: X-ray Diffraction Pattern For Dolomite Samples (F).

Table 3.4: Physical Characteristics Of The Samples.

Mineral	Particle Size, μm	Pore Size, Å	Surface Area, m^2/g	Porosity %
Sample	d_{50}	Mean	BET	
Apatite	3.93	195	21.4	21.3
Dolomite A	10.58	178	10.4	13.1
Dolomite B	7.25	226	12.2	8.2
Dolomite C	9.4	194	7.61	5.2
Dolomite D	7.81	176	9.74	6.3
Dolomite E	8.87	85	2.9	2.9
Dolomite F	4.26	120	2.06	1.8

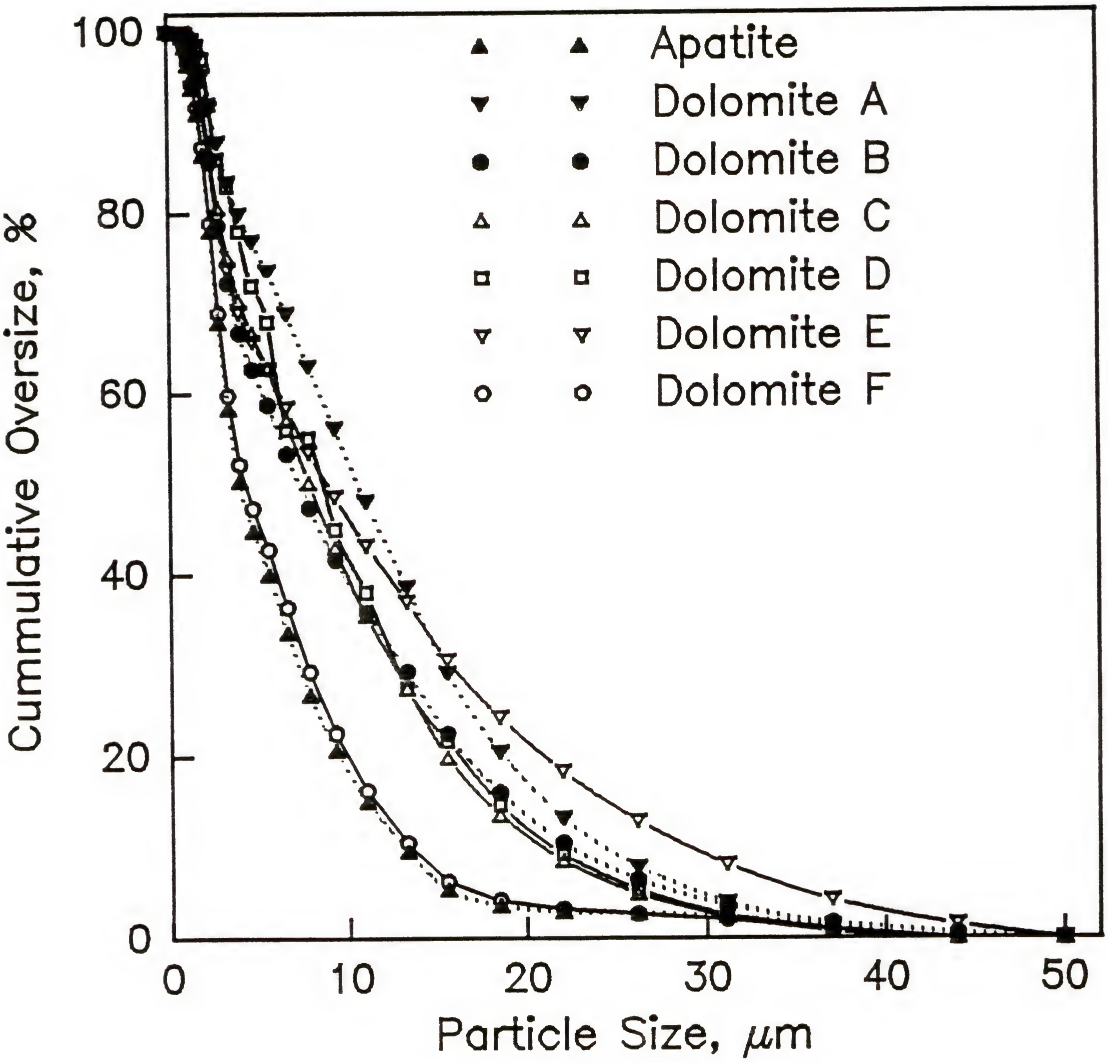


Figure 3.5: Particle Size Distribution Of The Various Samples.

Surface area and porosity

The surface area and pore size distribution of the various samples were determined by Autosorb micromeritics ASAP 2000 system. The surface area was estimated by the BET method using adsorption and desorption of nitrogen and is given in Table 3.4. Relatively higher specific surface area of apatite and most of dolomite samples indicate that the samples were highly porous. The pore size distribution for the samples is given in Figure 3.6. The mean pore size varies from 85 to 226 Å (see Table 3.4).

Scanning electron microscopy

SEM (Jeol JSM6400) micrographs presented in Figures 3.7-3.10, show the morphology of the particles. Dolomite particles (sample A,B,C,D) have a rougher surface compared to the other samples, which could be the other reason (other than porosity) for the very high surface area of these samples.

Surface Chemical Characterization

The surface chemistry plays an important role in adsorption and flocculation. The particle surface was characterized for charge and surface chemical groups. Further the surface charge characteristics of apatite and dolomite exhibit aging behavior in solution. A number of previous studies [Cha86, Mou87a] have shown that the aging behavior is fairly complex especially when the initial pH is acidic. It was found by Ince [Inc87] and Shah [Sha86] that if the natural pH is not disturbed significantly (± 1 unit), the suspension reaches a pseudo-equilibrium within one hour of aging.

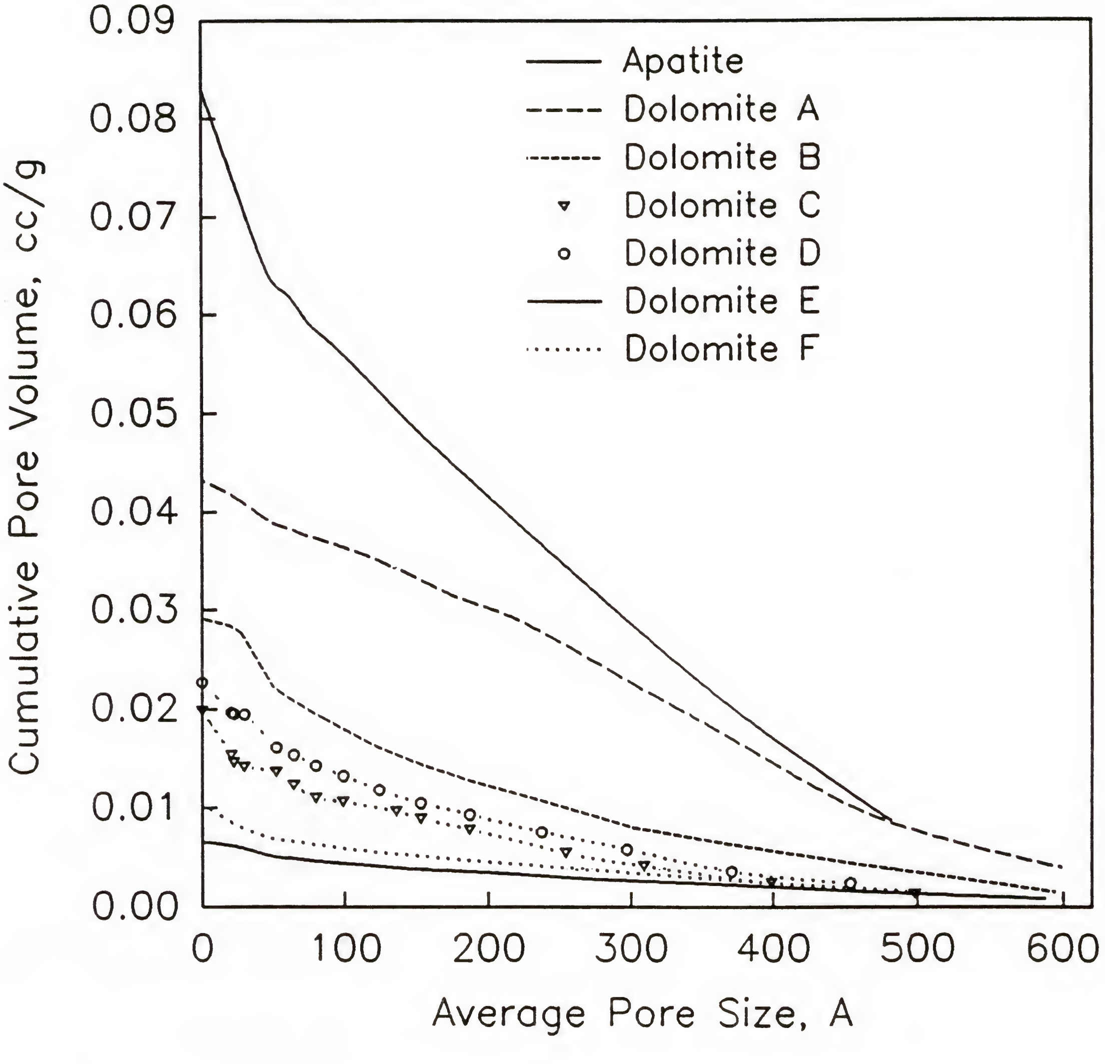
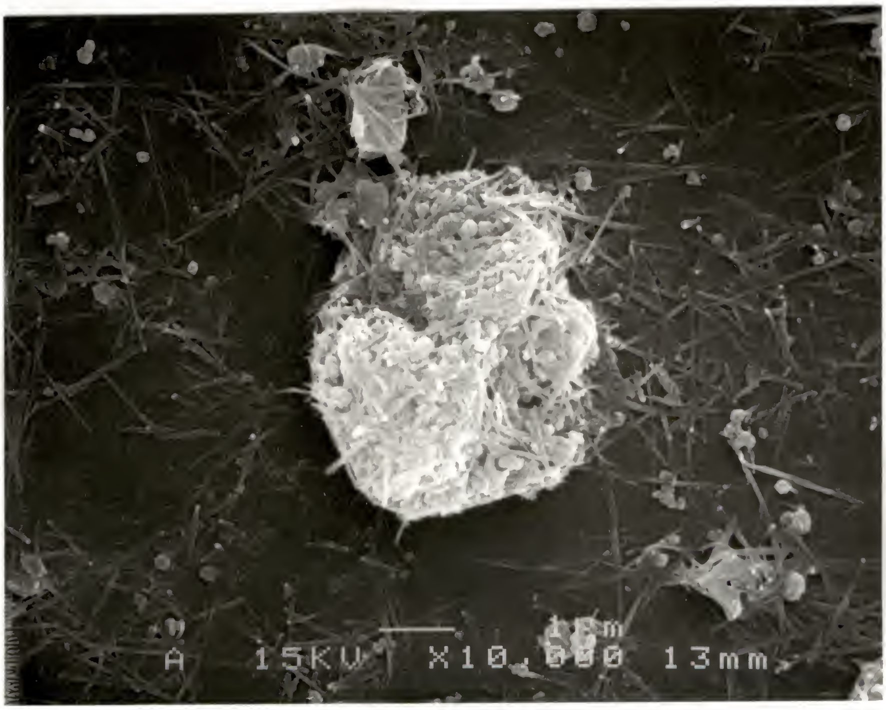
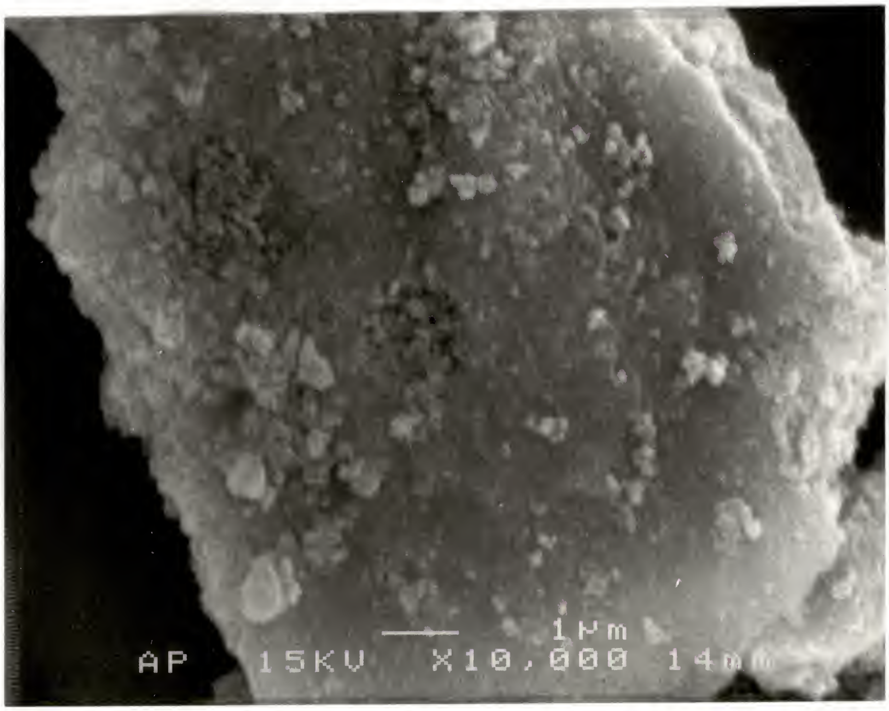


Figure 3.6: Pore Size Distribution Of The Various Samples.

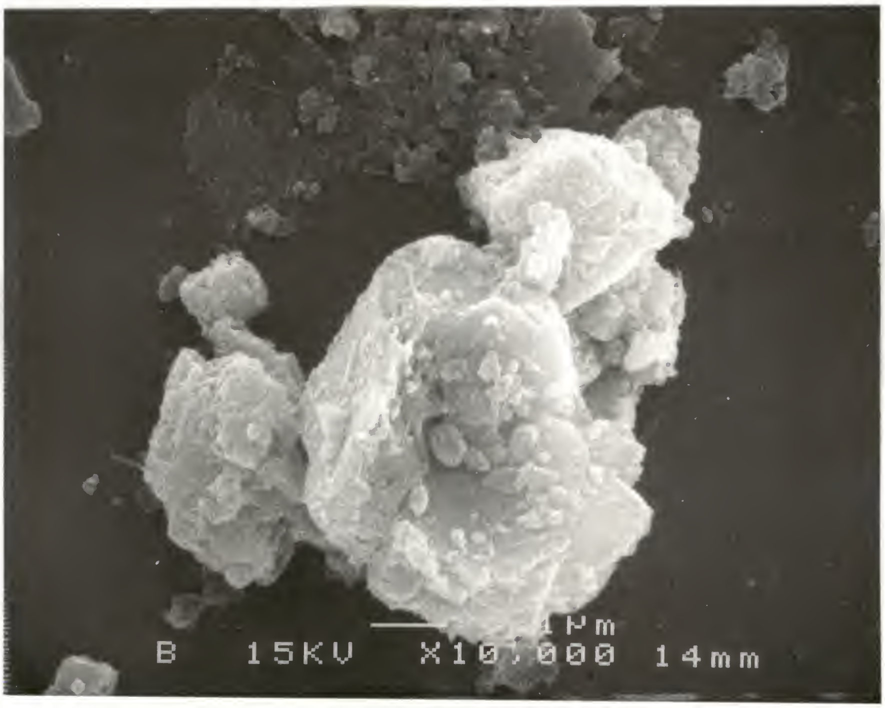


Dolomite A

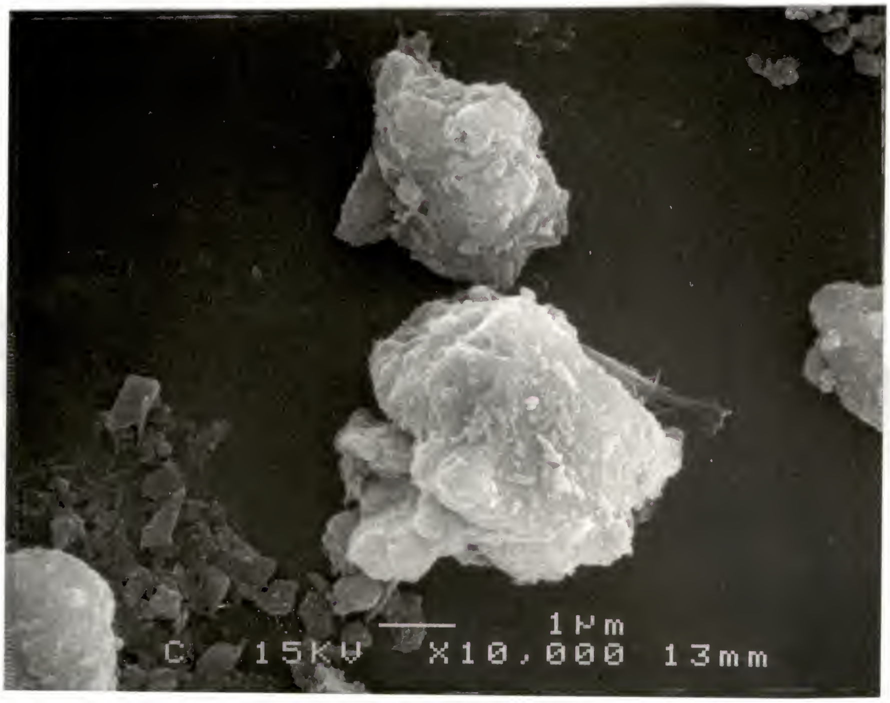


Apatite

Figure 3.7: SEM Micro-graphs Of Dolomite (A) And Apatite Particles. (10,000X)

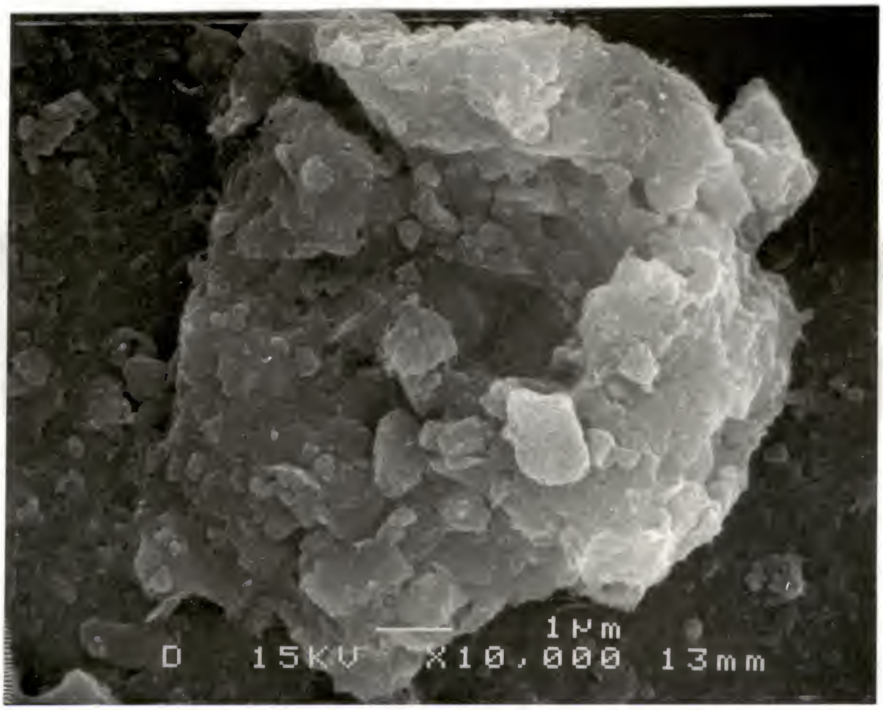


Dolomite B

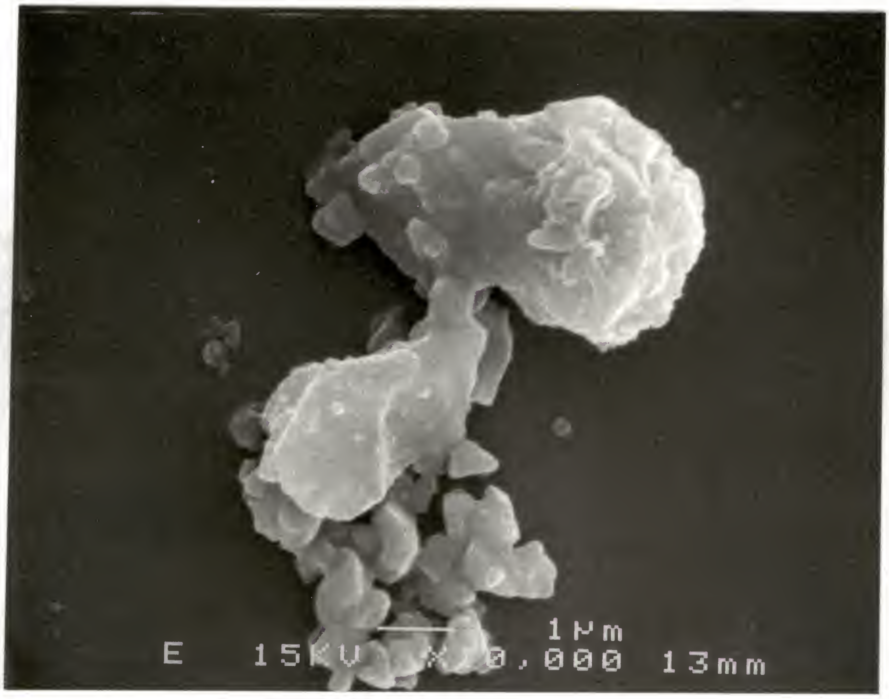


Dolomite C

Figure 3.8: SEM Micro-graphs of Dolomite Particle (B and C). (10,000X)

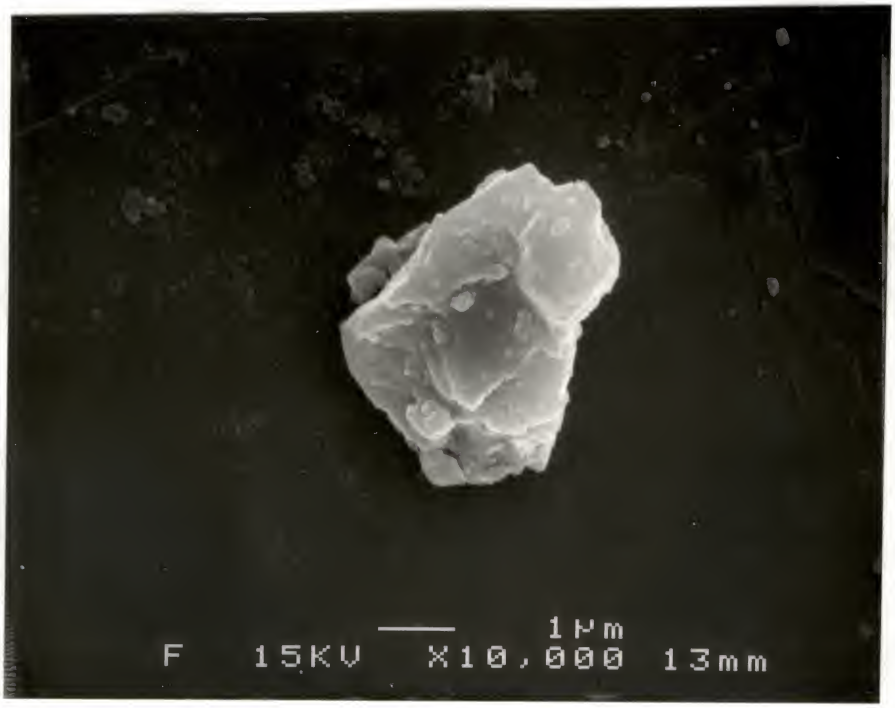


Dolomite D



Dolomite E

Figure 3.9: SEM Micro-graphs of Dolomite Particle (D and E). (10,000X)



Dolomite F

Figure 3.10: SEM Micro-graphs of Dolomite Particle (F). (10,000X)

Electrokinetic studies

Zeta potential was measured using the Laser Zee Meter (Pen Kem Model 501). 50 mg of the solid sample (less than 38 microns) was suspended in 100 ml of DI water (in certain cases 0.001M sodium silicate was added) and the solution aged for one hour. The pH was adjusted to a desired value and the sample aged for one hour. The suspension was then sonicated for 30 seconds and the final pH was recorded. After this about 50 ml of the sample was drawn and zeta potential measured.

Infrared studies

Samples used for FT-IR analysis were prepared by mixing a 0.05 g of vacuum dried sample with about 1.5 g of potassium bromide (KBr). This mixture was then filled in a sample cup mounted on a diffuse reflectance stage. The IR spectra was taken using a Nicolet 740 spectrometer. The beam was aligned for every sample to yield a maximum signal and further the baseline was adjusted using the software. This base line adjustment enabled a quantitative comparison of different spectra.

Dispersion Studies

Stability of single component suspensions was studied by measuring the settling rates of the solids. The experimental set up consisted of a microscope with a micrometer disc in the eye piece with a least count of 0.1 mm. The pre-aged samples were transferred to a 100 ml graduated cylinder after sonication. The cylinder was manually inverted ten times and placed on a horizontal base. The level of the sediment was monitored using the microscope.

Flocculation Studies

Flocculation apparatus

It has been reported that flocculation is sensitive to the type of agitation used [Hog85]. Hence it is necessary to maintain uniform, hydrodynamic conditions in all the experiments. The mixing unit employed in this investigation is based on the standard tank design [Dir81]. Dimensions of the mixing tank are given in Table 3.5. This tank ensures a constant turbulence, power consumption and flow pattern. The four baffles suppress vortex formation and minimizes power consumption.

A 150 ml beaker fitted with removable plexiglass baffles of appropriate dimensions was used for flocculation tests. A stainless steel turbine impeller with four blades mounted on a variable speed motor was employed to agitate the sample.

Flocculation procedure

The mineral suspension of the required pulp density was prepared in DI water using sodium silicate as a dispersant and aged for one hour. Sodium silicate dosage of 5 kg/t of solids (100 ppm or 3.5×10^{-4} M; see next chapter for details) was determined to yield a dispersion. Based on previous work [Mou87a] the maximum pH variation after pre-aging in the alkaline pH range was determined to be 0.2 pH units. After aging, the mineral was agitated at 1100 rpm, for 240 seconds while the pH was adjusted to 9.50 throughout the study. The suspension was then sonicated for 30 seconds to ensure complete dispersion and a pre-determined amount of polymer was added. In certain cases, the suspension was conditioned with a desired dosage of SBA for 420 seconds prior to flocculant addition. The agitation was continued for 120 seconds within which

Table 3.5: Dimensions Of The Flocculation Cell.

Flocculation Cell Part	Dimension, cm
Tank Diameter	6.2
Impeller height from tank bottom	0.5
Impeller blade width	1.6
Liquid height	4.6
Baffle width	4.0

the flocculation was observed to be complete. The flocs were separated from the suspension, dried at 110 °C overnight, weighed and analyzed using ICP.

Separation of flocs. The method of separation of flocs from the suspension is very important, as this forms the basis of evaluating the efficiency of separation. Since the major aim of this study was to understand the selectivity in floc formation, separation was achieved by sieving the flocs through a 400 mesh screen. The other methods for separation of flocs such as sedimentation and floc floatation are strong function of the floc properties [Kri85, Att88b, Att88c] and could, therefore, lead to misleading results.

Analysis of the mixture. After flocculation, it is necessary to determine the composition of the flocs and the dispersed material. One gram of accurately weighed solids was digested with 25 ml of dilute aqua regia (20 %) on a hot plate for 30 minutes. The digested sample was filtered using a Whatman #5 filter paper and diluted to 1000 ml. A 20 ml solution was drawn from the diluted sample and analyzed for calcium and magnesium using a Perkin Elmer, inductively coupled plasma (ICP) emission spectrometer. In cases were the sample to be analyzed was less than one gram, the above procedure was followed and the ICP results were normalized.

Polymer Solution Preparation. 500 ppm PEO (wt/vol) of molecular weight 5 million was prepared fresh everyday for the experiments since changes were observed in PEO when stored for more than one day [Mou92]. The polymer solutions were protected from UV light while stirring and during storage by covering the flask with brown paper. The lower molecular weight polymers were prepared at a concentration of 1000 ppm. This was required because the amount of lower molecular weight polymer used was much higher than the 5 million PEO.

Adsorption Studies

Adsorption of the polymer on the single minerals was carried out in the supernatant of the other, to account for the ion interference. Both equilibrium and non-equilibrium isotherms were generated. The equilibrium isotherm was needed to quantify the total adsorption possible on the surface to estimate the surface active site ratio (Φ). On the other hand, the non-equilibrium isotherm was carried out to determine the adsorption of the polymer under the flocculation conditions (θ).

Equilibration time for PEO molecule (molecular weight 5×10^6) was determined to be within 16 hours for both apatite and dolomite (see Figure 3.11 and 3.12). Although a much smaller equilibration time on apatite was observed, for the purpose of this study the polymer was contacted with the solids for 16 hours irrespective of the nature of substrate. Further, the lower molecular weight PEO adsorbed much faster, however, in this case also 16 hours contact time was used. Adsorption was carried out in dark bottles (flasks) by contacting the polymer solution with solids in a revolving shaker. After equilibration the sample was centrifuged at 12,000 rpm for 6 minutes and the supernatant drawn. The residual PEO was determined by either total carbon analyzer (TOC) or by viscometry. Adsorption was determined by the depletion method. Considering the scatter in the adsorption data, the saturation adsorption value was obtained by fitting the Langmuir equation for high concentrations [Att91].

In case of non-equilibrium adsorption, the flocculation procedure was followed to have identical contact time to determine the surface coverage. At the completion of the experiment the supernatant was centrifuged and the residual concentration in the

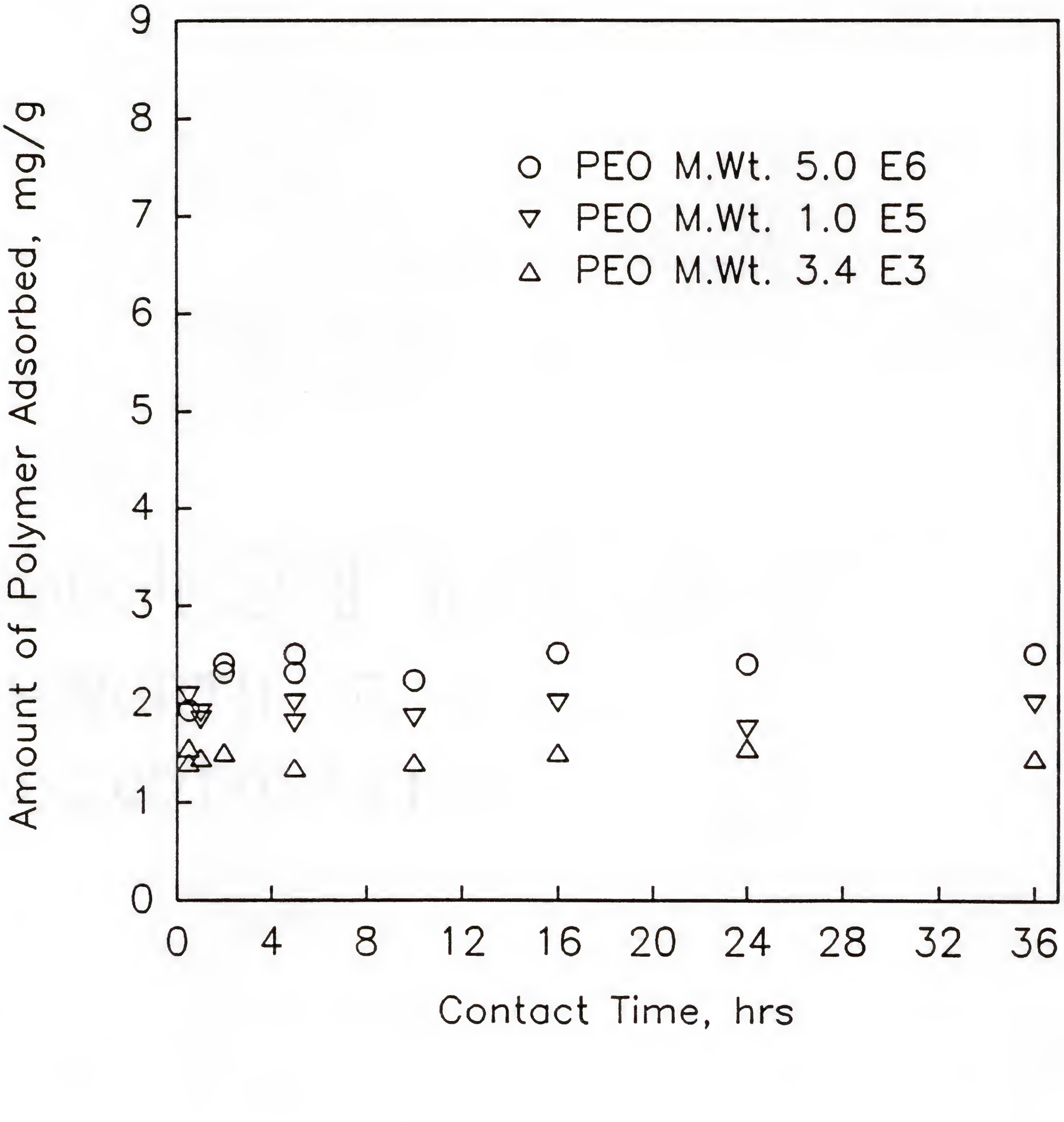


Figure 3.11: Equilibration Adsorption Time For PEO/PEG On Apatite.

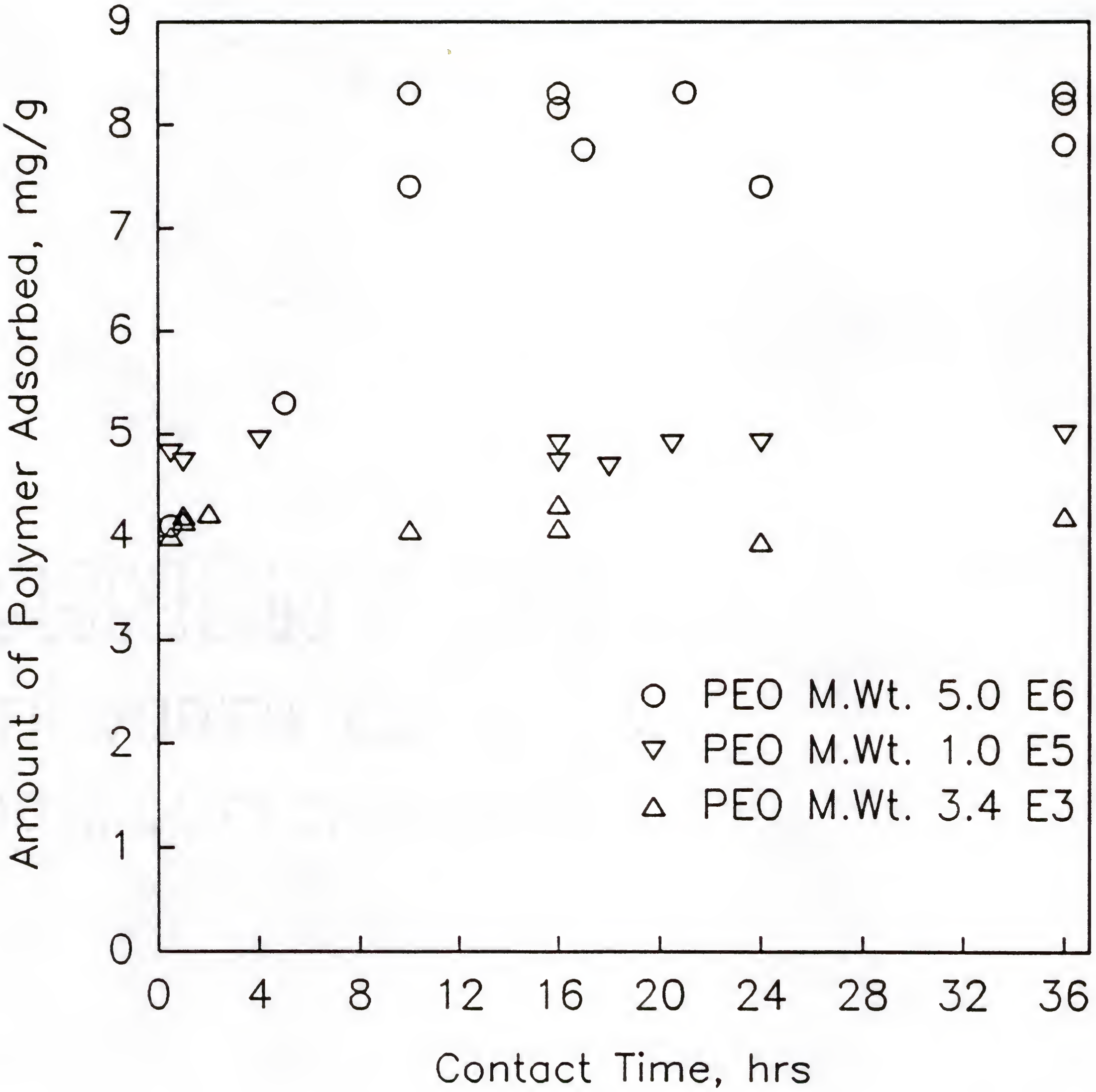


Figure 3.12: Equilibration Adsorption Time For PEO/PEG On Dolomite.

supernatant measured by either TOC or viscometry.

Poly(ethylene oxide) Analysis

It is necessary to analyze residual concentration of PEO/PEG when adsorption isotherm of the polymer on the various minerals are generated using the solution depletion method. The analysis of the dilute polymer solution was performed using total organic carbon (TOC), however, for the higher molecular weight PEO, viscometry techniques could also be employed [Mou86, Sha86]. For concentration range between 0 to 100 ppm both of these methods are in very good agreement and no significant ion interference was observed [Mou86]. However, it must be noted that supernatant of the minerals used in the study had an appreciable (up to 3 ppm) of total organic carbon, which had to be taken into account in computing the adsorption on the substrates.

Total organic carbon analysis method Total organic carbon concentration analysis was performed using a total organic carbon analyzer (Ionics model 1555). 10 microliter of the solution was injected in the system and the net response noted. The system was first calibrated with a standard solution in the range between 0 and 12 ppm of total organic carbon. Standard solutions of PEO or PEG were made in the supernatant of the minerals and then calibrated against the standard solutions. The same procedures were followed for analysis of the samples. Further, some samples were diluted from higher concentrations to measurable values of 12 ppm. The calibration chart for PEO in water for different molecular weights is given in Figure 3.13. Also the solid samples had initial carbon content in the supernatant. The calibration charts for PEO in dolomite and apatite supernatant are presented in Figure 3.14. A very good straight line regression may be performed on the data. It was observed that the TOC of DI water was 0.7 ppm.

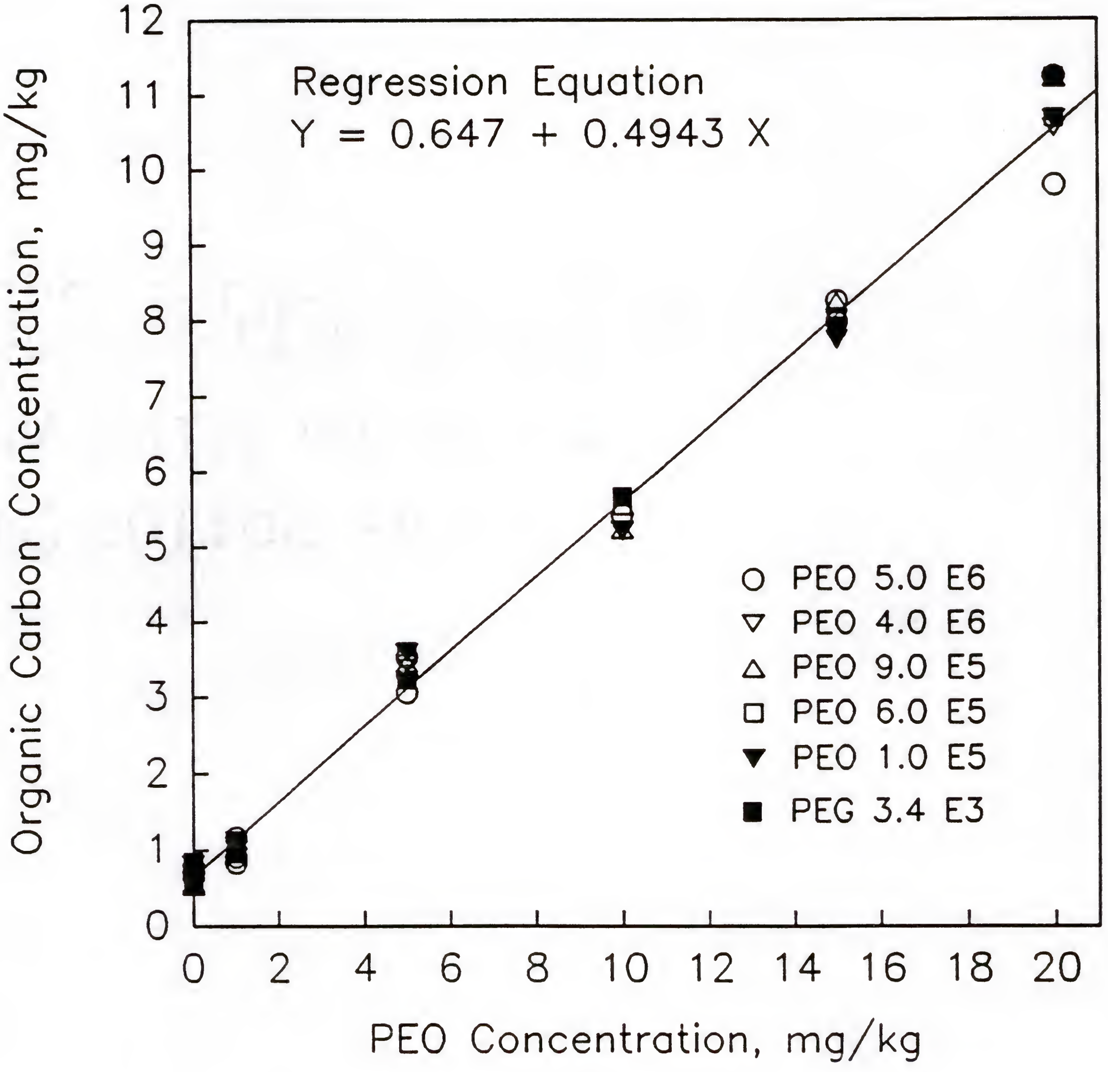


Figure 3.13: Total Organic Carbon Calibration Of Various Molecular Weights Of PEO.

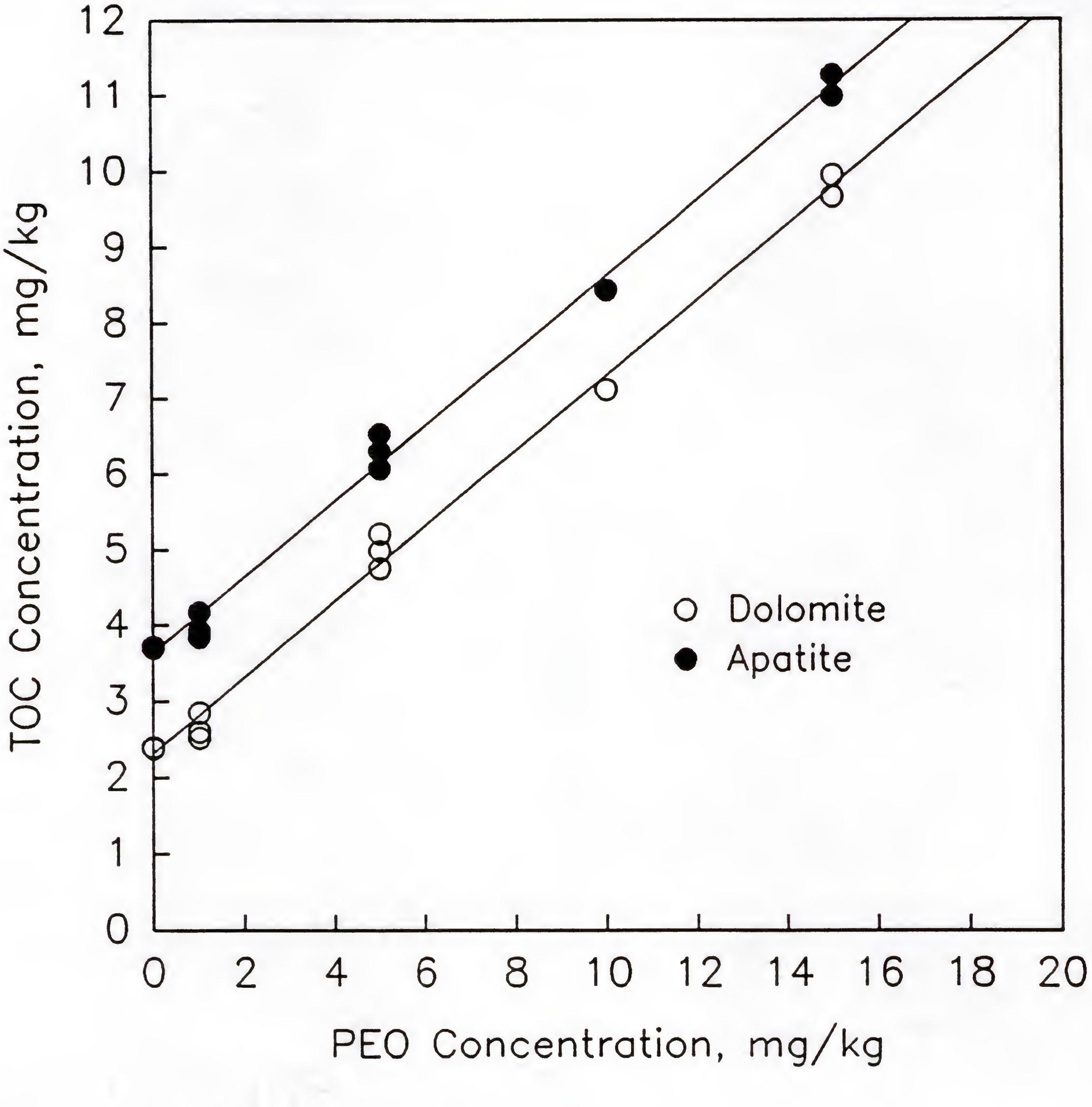


Figure 3.14: Total Organic Carbon Calibration of PEO in Apatite and Dolomite Supernatant.

The precision of the equipment was ± 0.25 ppm. The regression equation for PEO/PEG calibration in supernatant of different dolomite's is given in Table 3.6.

Viscosity method The viscosity measurements of the polymer (PEO of molecular weight 5 million) solution were made using Ubbelohde Capillary Viscometer (No. OB 34). The viscosity of the polymer was monitored by determining the efflux time of a fixed volume of the solution to pass through the capillary in the viscometer suspended in a constant temperature bath maintained at 30 ± 0.1 °C. The efflux time was measured to an accuracy of 0.01 seconds.

The time required for water to pass through the capillary was determined to be 191.52 seconds. Standard PEO solutions with concentrations between 0 to 100 ppm were prepared and their efflux time recorded. The linear calibration curve obtained by plotting efflux time (t) as a function of the polymer concentration is shown in Figure 3.15. The precision of this method was ± 2 ppm. The precision for lower molecular weights was much lower and infact for 100,000 molecular weight the precision was found to be ± 25 ppm, thus limiting this method to only higher molecular weights. The intrinsic viscosity of 5×10^6 is 19.99 dl/g while that of 1×10^5 is 0.99 dl/g [Bai76]. It is known that the intrinsic viscosity has a straight line variation as a function of concentration, therefore, the effect of small amounts of lower molecular weight polymer in the solution of 5 million molecule will not show up in the viscosity measurements. For example, on mixing 25 ppm of 100,000 molecular weight PEO with 5 million molecular weight polymer solution, no change in the viscosity was observed. This property combined with the total organic carbon analysis enabled the detection of higher molecular weight polymer in the presence of lower molecular weight fraction.

Table 3.6: Calibration Equation For Polymer Concentration By Total Organic Carbon Analysis.

Mineral	Regression Equation; $Y = Ax+B$
Apatite	$Y = 0.4943 X + 3.07$
Dolomite A	$Y = 0.4943 X + 1.69$
Dolomite B	$Y = 0.4943 X + 1.71$
Dolomite B	$Y = 0.4943 X + 1.71$
Dolomite D	$Y = 0.4943 X + 2.31$
Dolomite E	$Y = 0.4943 X + 1.51$
Dolomite F	$Y = 0.4943 X + 1.45$

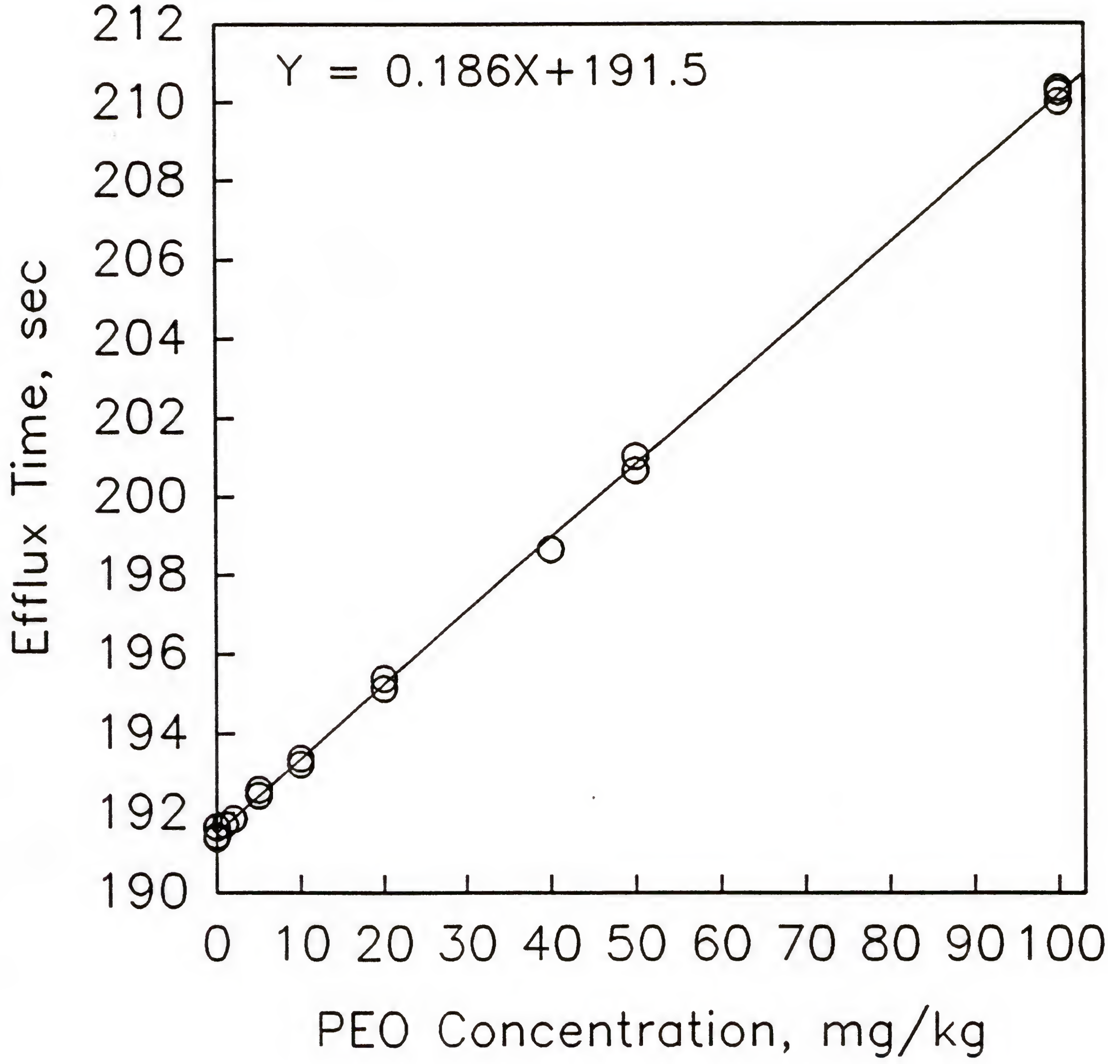


Figure 3.15: Calibration Curve For Measurement Of PEO (Molecular Weight 5 Million) Concentration By Viscometry.

Heat Of Adsorption Studies

The heat of adsorption of the polymer was measured using a Setaram C-80 heat flux microcalorimeter. The microcalorimeter was initially set to the desired temperature using the temperature programmer/controller so as to have an isothermal mode of operation. Membrane cells were used to mix the polymer solution with the solid slurry. The membrane cell consists of two compartments separated by an aluminum membrane. The bottom compartment of the sample cell was filled with 2 ml 50 ppm of PEO. 16 wt % slurry was prepared with the required amount of sodium silicate at pH 9.5. One ml of this slurry was kept in the top compartment of the sample cell. This configuration eliminates the need to evaluate the heat of wetting or immersion of the dry mineral. A reference cell was prepared that was identical to the sample cell with the exception of the solid. The heat effect due to dilution of the polymer solution was minimized by this arrangement. In this case the heat of adsorption would be identical to the excess heat. This arrangement is similar to that of Cohen-Stuart et al. [Coh84]. Both the cells were then loaded into the microcalorimeter. Thermal equilibrium was attained within 2-3 hours and was indicated by a steady baseline signal on the computer screen. Impellers connected to each of the cells were used to pierce the aluminum foils simultaneously and stirred 5 times so as to insure proper mixing of the solid and the polymer solution. The experiments were normally carried out for a duration of 30-45 minutes until a steady baseline signal was once again observed.

One of the two major limitations of the above experimental set up is that concentrated slurries and high polymer dosages cannot be used because of higher viscosity and possibly uneven mixing. The other limitation involves flocculation of the solids since the polymer can act as a flocculant. In the present case apatite does not flocculate with PEO, while dolomite does. To minimize the effect of flocculation, the solids are kept in the top chamber and are introduced in the polymer solution. Since the stirring is controlled, the particle-particle collisions are limited and floc formation is minimized. The flocculation is also reduced by using very dilute suspensions. The adsorption of the polymer on the aluminum membrane (foil) surface is expected to be insignificant since the surface area exposed is extremely small.

To study the heat of dilution of PEO in the supernatant experiments, the suspension was first centrifuged at 10,000 rpm for 10 minutes to remove the solid particles. The other experimental conditions were kept constant to minimize other heating effects.

The good reproducibility (within ± 5%) of the measured heat of adsorption values can be attributed to the very precise temperature control in the instrument.

CHAPTER 4
SELECTION OF VARIABLES AND EXPERIMENTAL CONDITIONS

Introduction

Experimental data for the purpose of selecting the relevant variables and operating conditions for separation of apatite from dolomite by selective flocculation is described in this chapter.

Dissolution Studies

It is well known that apatite and dolomite have significant dissolution in the acidic pH range. These studies were carried out to identify conditions, where dissolved ions in the suspension will have minimal effect on polymer adsorption and subsequently flocculation. The dissolution of apatite and dolomite was monitored by measuring the concentration of calcium ions in the supernatant. It can be seen from the Figure 4.1 that above pH 9.5 the concentration of calcium ions in the supernatant is low. This agrees with the earlier data reported by Ince [Inc87] and Attia and Fuersteaneau [Att88/89].

Dispersion Studies

The electrokinetic behavior of apatite as shown in Figure 4.2, follows the trends reported earlier [Cha86, Inc87]. The low zeta potential values may be attributed to high ionic strength present in the system due to a significant dissolution of the mineral. The electrokinetic data indicate that apatite may not be dispersed without a suitable

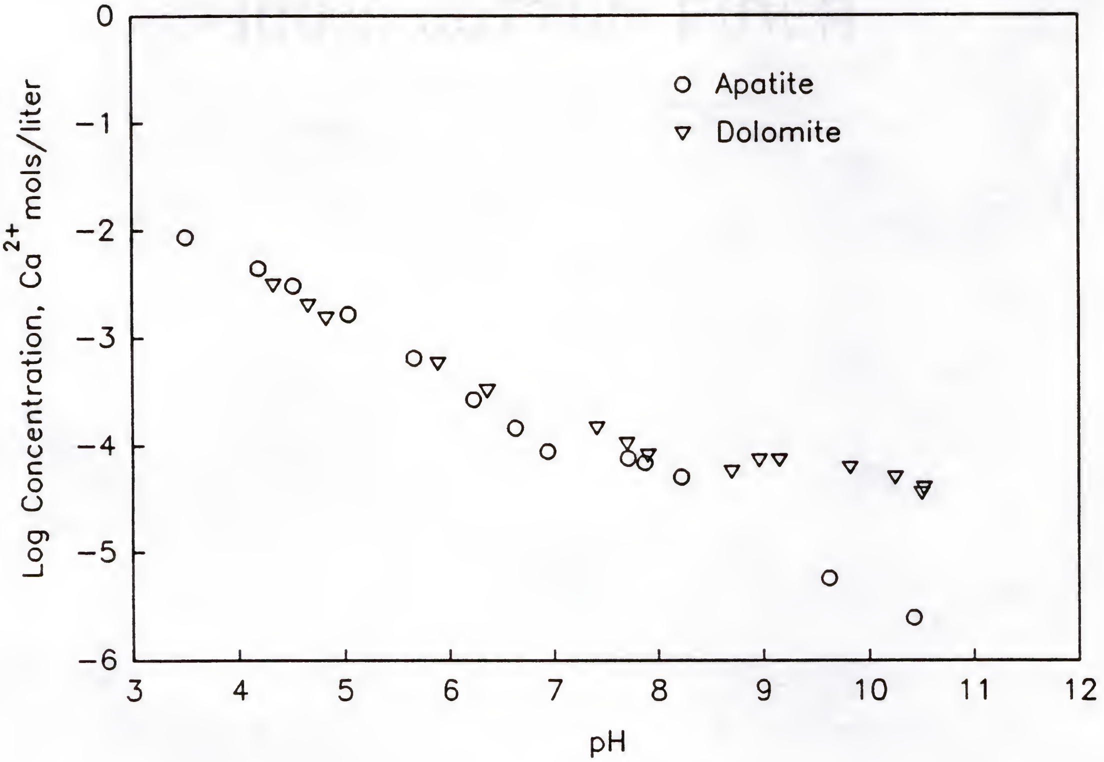


Figure 4.1: Dissolution Of Apatite And Dolomite As A Function Of pH.

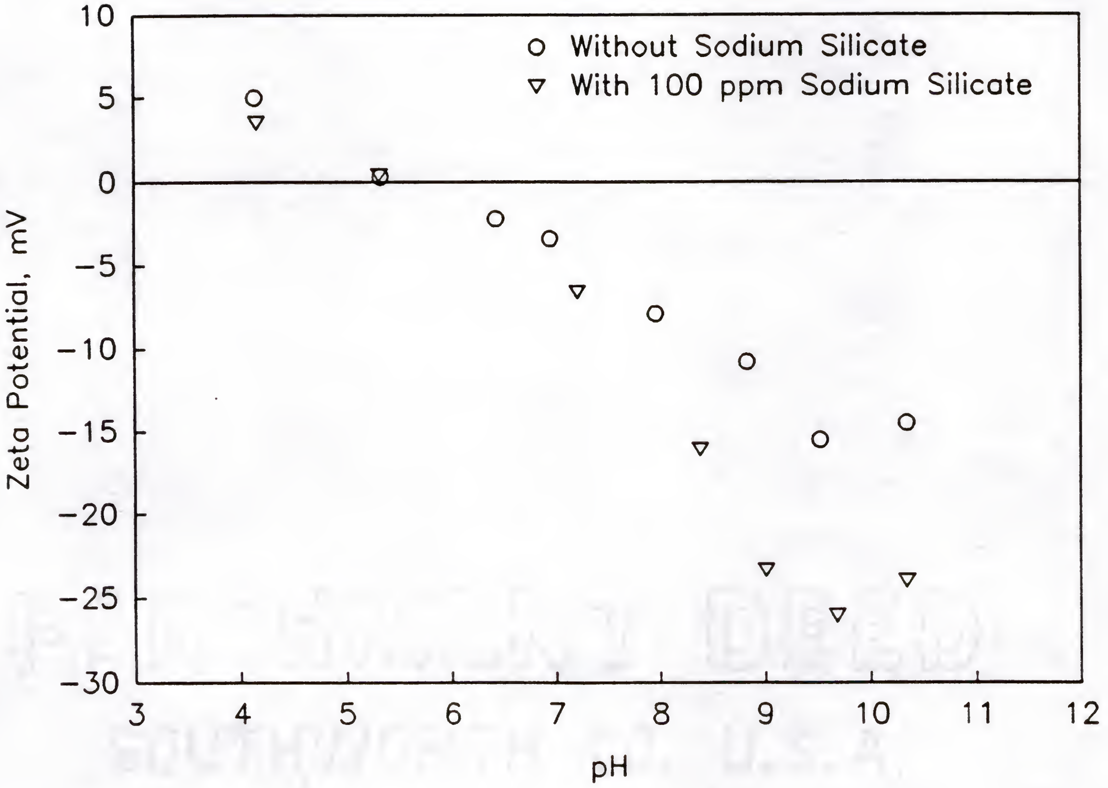


Figure 4.2: Zeta Potential Of Apatite As A Function Of pH.

dispersant. It was reported earlier by Shah [Sha86] that sodium silicate is a good dispersant for apatite. It can be seen from Figure 4.2 that the zeta potential value in the presence of sodium silicate around pH 9.5 is fairly high and apatite should be dispersed under these conditions. The extent of dispersion was assessed by settling tests. It can be seen from Figure 4.3 that a dispersant dosage of 5 kg/t is suitable for dispersing the apatite suspension. Dolomite sample on the other hand can easily be dispersed at pH 9.5 with and without sodium silicate as is clear from the zeta potential and settling results (see Figures 4.4 and 4.5).

It is clear from the above that both apatite and dolomite can be dispersed at pH 9.5 with sodium silicate as a dispersant.

Single Mineral Flocculation Studies

Selection Of The Flocculant

The first step in the selective flocculation process is to identify a polymer that would flocculate only one of the components of the mineral mixture. The selection of the flocculant is often done by hit and trial method.

It is well known that adsorption is a pre-requisite for flocculation, therefore, some indication of the nature of the polymer to be used, can be attained by studying the surface of the mineral, instead of choosing the flocculant arbitrarily. It can be seen from the diffuse reflectance FTIR spectra of the minerals in Figure 4.6, that isolated hydroxyl groups (3619 cm^{-1}) exist on the dolomite surface and physical adsorbed water (3400 cm^{-1}) on the surface of apatite. Rubio and Kitchner [Rub76] and Cheng [Che85] have shown that PEO is an excellent flocculant for a material with isolated hydroxyl groups.

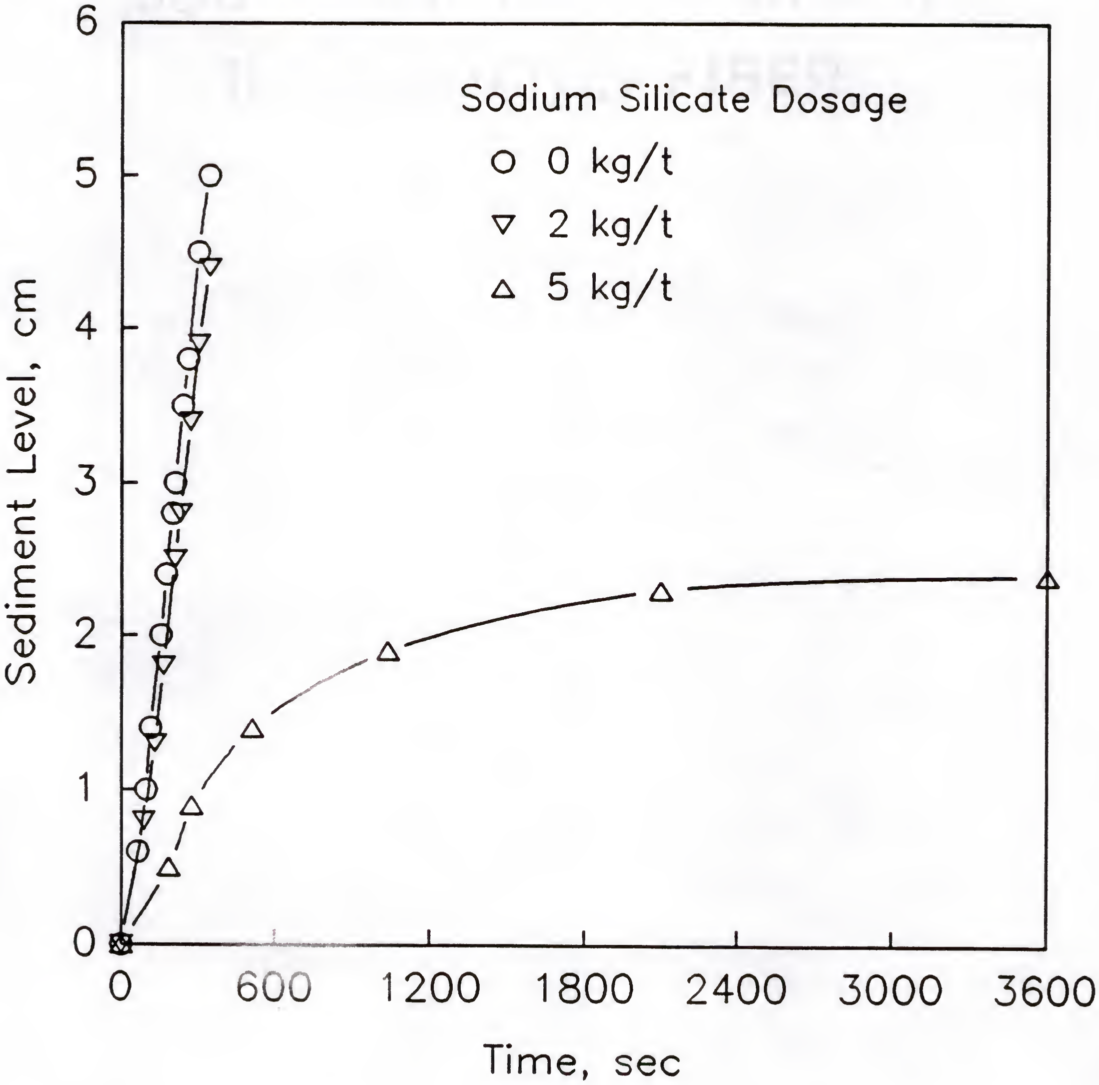


Figure 4.3: Settling Behavior Of Apatite Slurry.

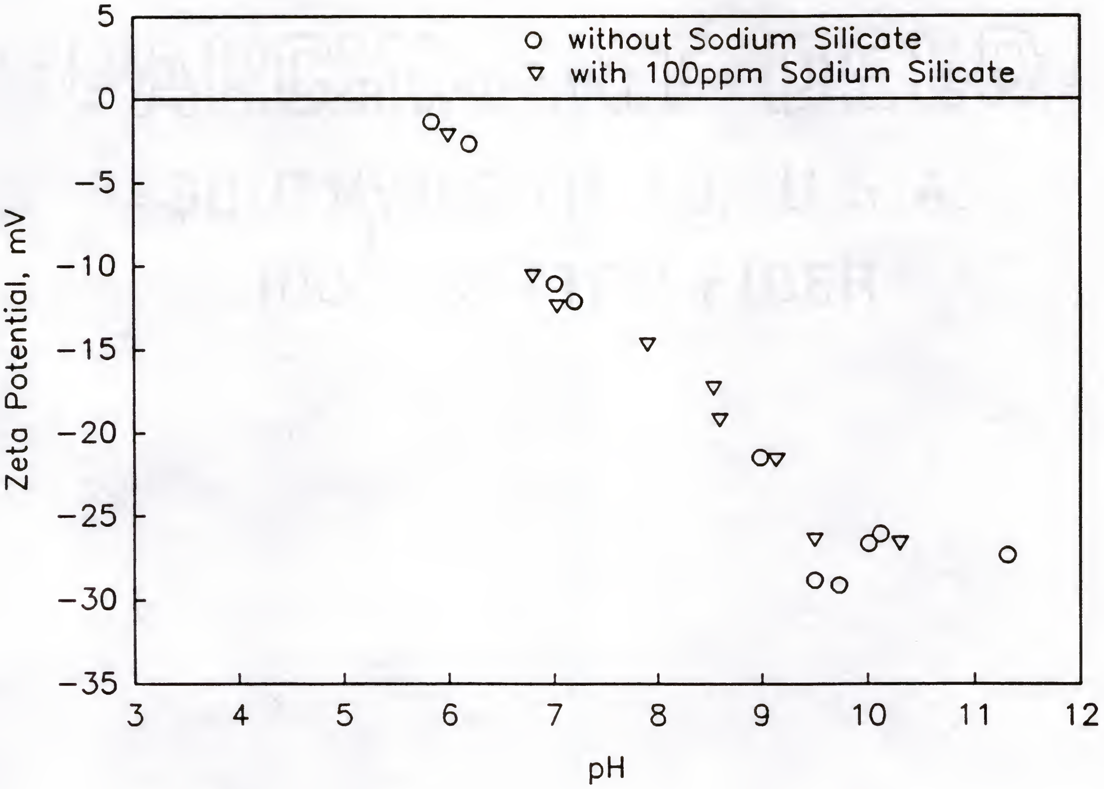


Figure 4.4: Zeta Potential Of Dolomite As A Function Of pH.

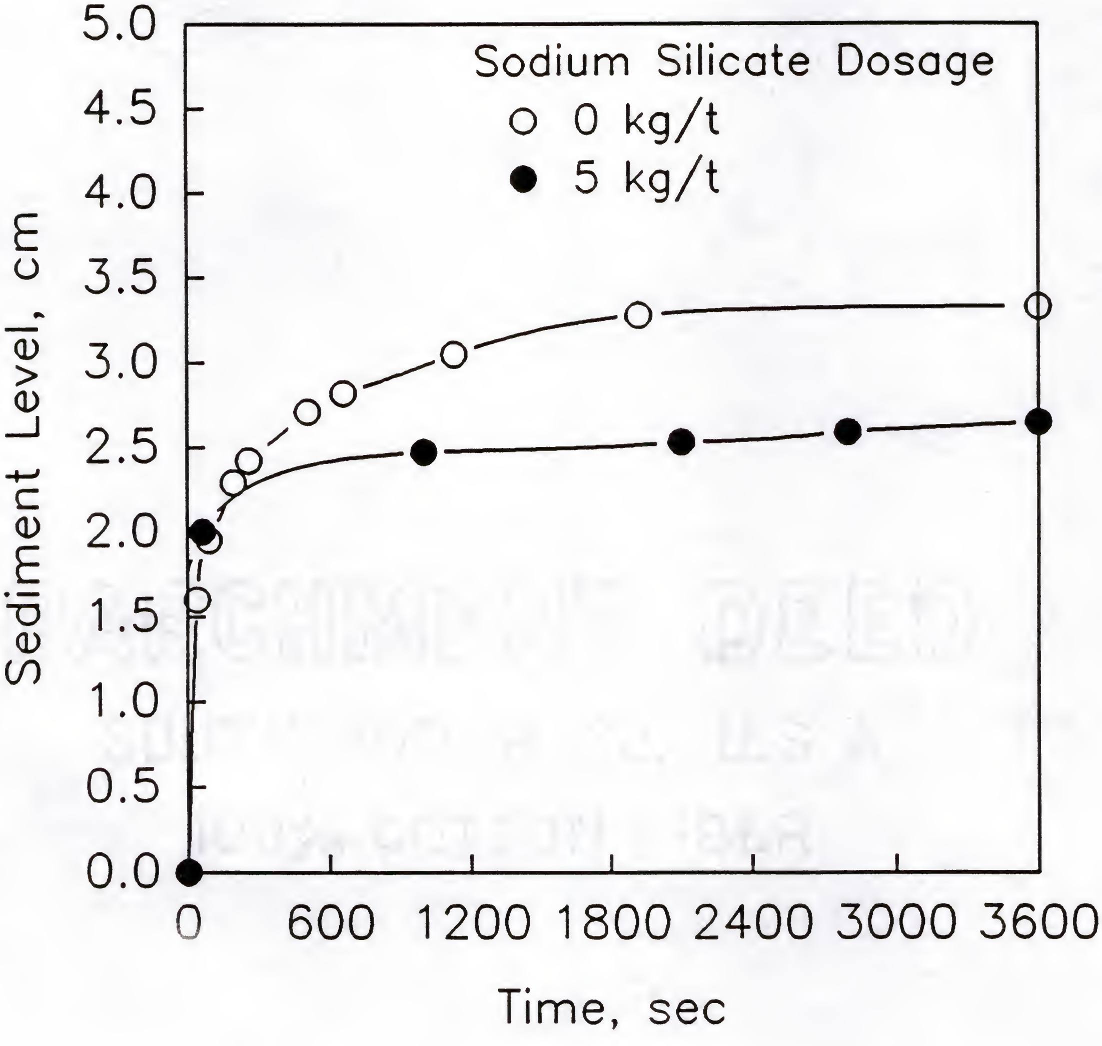


Figure 4.5: Settling Behavior Of Dolomite Slurries.

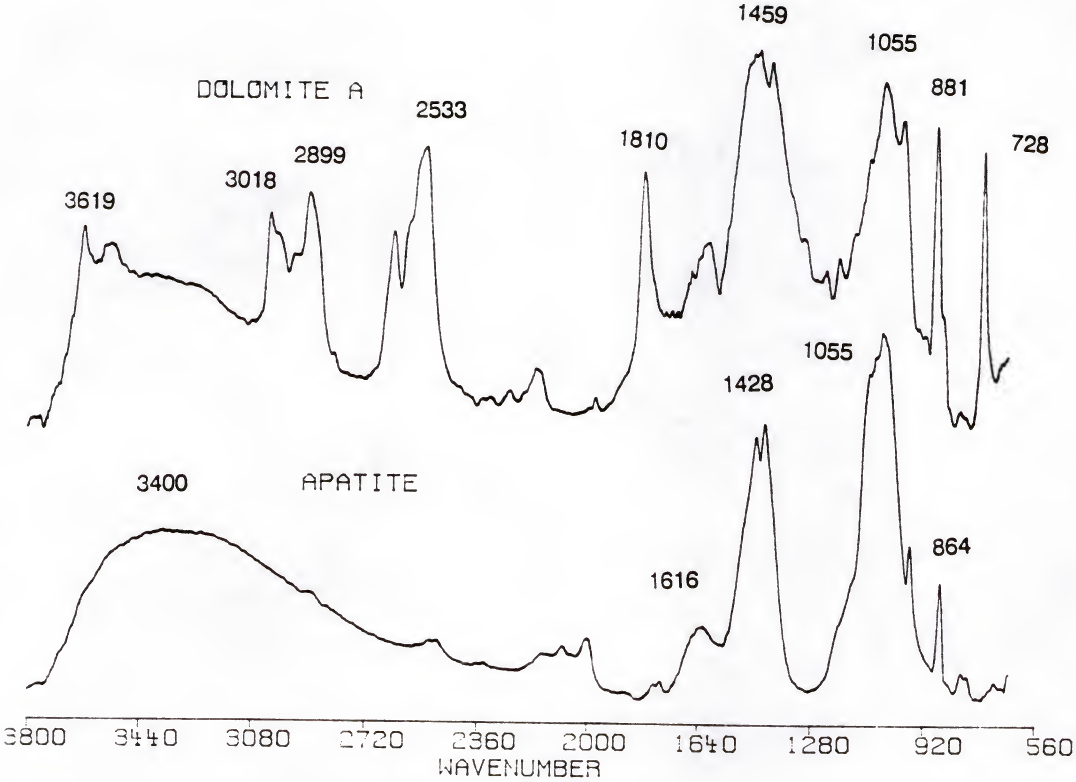


Figure 4.6: FT-IR Spectra Of Apatite And Dolomite.

Any polymer capable of hydrogen bonding such as polyacrylic acid (PAA), polyacrylamide (PAM), polyethylene oxide (PEO), etc., would be capable of flocculating the two materials. Among these, PEO is a weak flocculant [Sch87], therefore, only the material with a stronger interaction with the polymer molecule may be expected to flocculate. Preliminary flocculation results indicated that dolomite flocculated well with PEO of 5 million molecular weight while apatite did not exhibit any floc formation. This is in agreement with the previous results [Sha86].

Effect Of PEO Dosage

Experiments performed with poly(ethylene oxide) of 5 million molecular weight at pH 9.5 indicated that irrespective of the amount of polymer added, flocculation of apatite is not observed (see Figure 4.7). On the other hand, instantaneous flocculation was observed for dolomite. At a dosage of 1 kg/t (20 mg of polymer /kg of dry solids) the entire dolomite formed one big floc.

Effect Of PEO Molecular Weight

Dolomite flocculation tests were conducted using PEO of different molecular weight. As seen from Figure 4.8, at a dosage of 1.0 kg/t, flocculation starts at molecular weight of 900,000 and complete flocculation is achieved with 5 million molecular weight PEO. The lower molecular weight polymers, although known to adsorb on the solid particles, are not capable of flocculation. The reasons for this behavior are explained in Chapter 6.

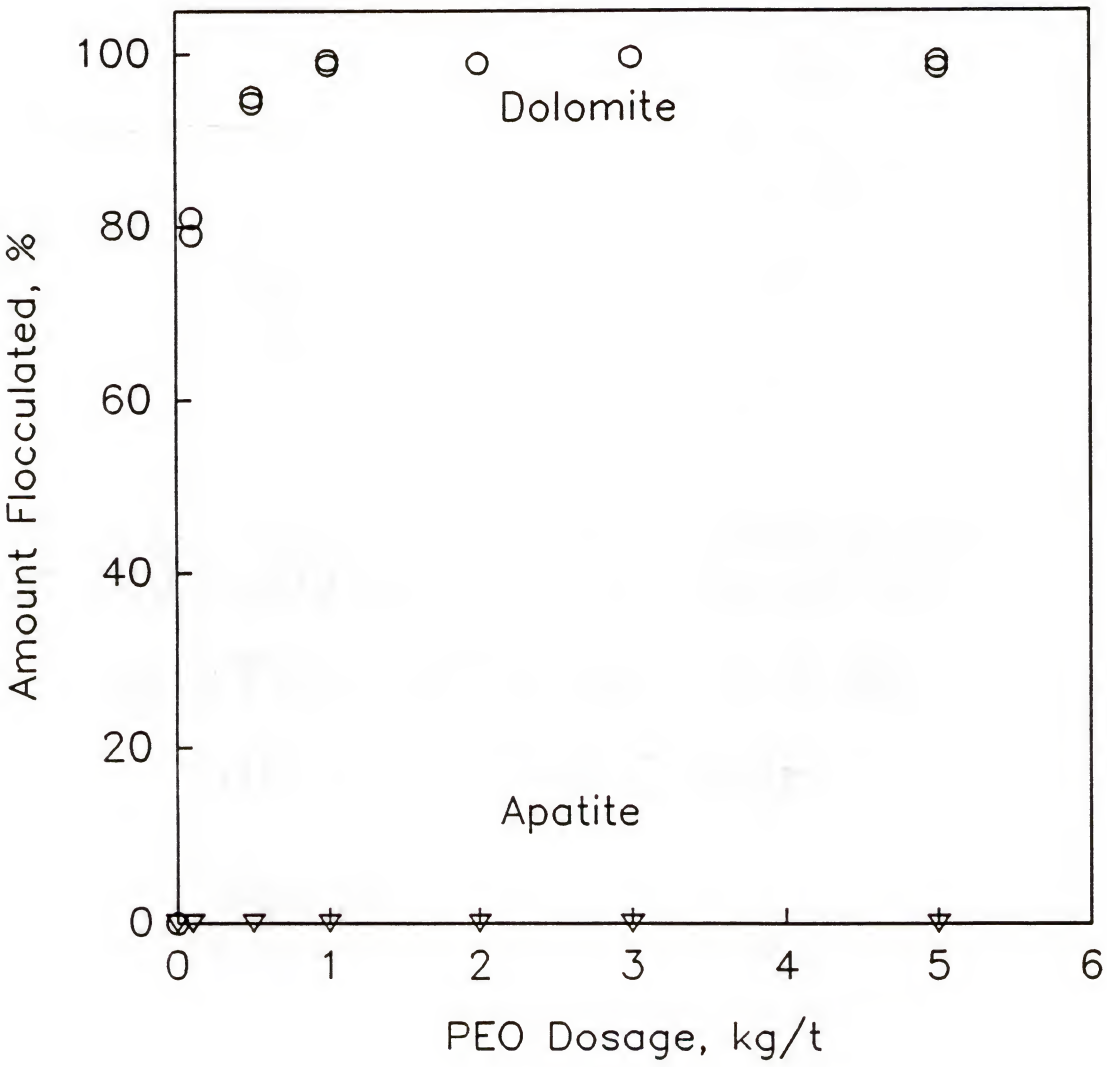


Figure 4.7: Single Mineral Flocculation Of Apatite And Dolomite As A Function Of PEO Dosage.

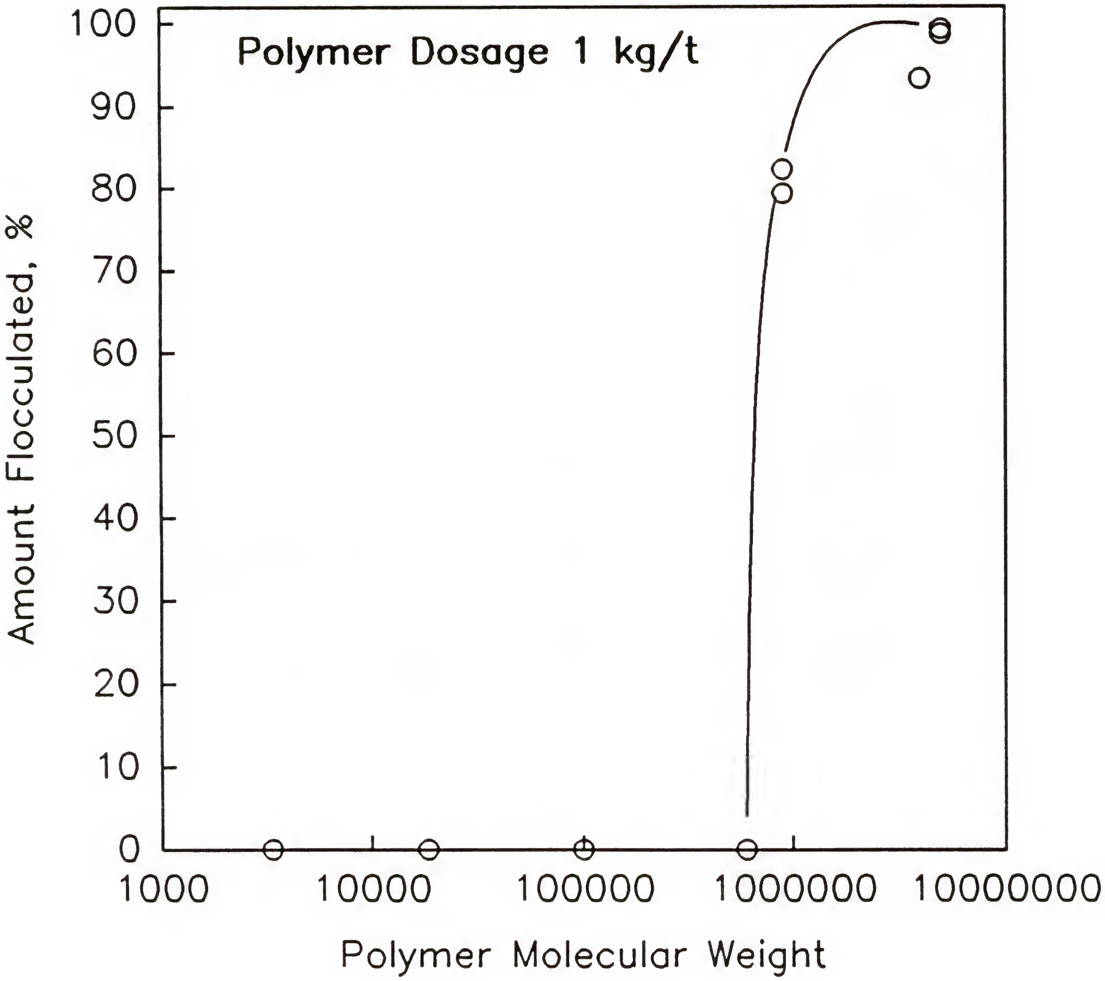


Figure 4.8: Effect Of Molecular Weight On Flocculation Of Dolomite.

Mixed Mineral Flocculation Studies

Effect Of Polymer Dosage

Mixed mineral flocculation tests were conducted using synthetic mixtures of apatite and dolomite as a function of polymer dosage. All experiments were carried out with PEO of 5 million molecular weight. Flocculation results in terms of grade and recovery of apatite in the concentrate, obtained with a 80:20 mixture (by weight) of apatite and dolomite are presented in Figure 4.9. Since dolomite is the flocculating component, low recovery of apatite (in the supernatant) at a constant grade, implies that much of the apatite flocculates and there is a loss in selectivity during floc formation. The separation of apatite from dolomite can also be evaluated in terms of separation efficiency,which is a measure of both selectivity and recovery. Separation efficiency[1] is higher at extremely low dosages of the flocculant and corresponds to slightly higher recovery and grade values (see Figure 4.9).

Effect Of Apatite/Dolomite Ratio

The effect of different ratios of apatite and dolomite was investigated for a flocculant dosage of 1.0 kg/t and the results are presented in Table 4.1. It can be seen

---

[1] Separation Efficiency = (SI X Recovery)/100 ; where
SI = 100 X (%Grade in Concentrate - % Grade in Feed)/(100-% Grade in Feed)
Recovery = (Amount of apatite in Concentrate/Amount of apatite in Feed) X 100

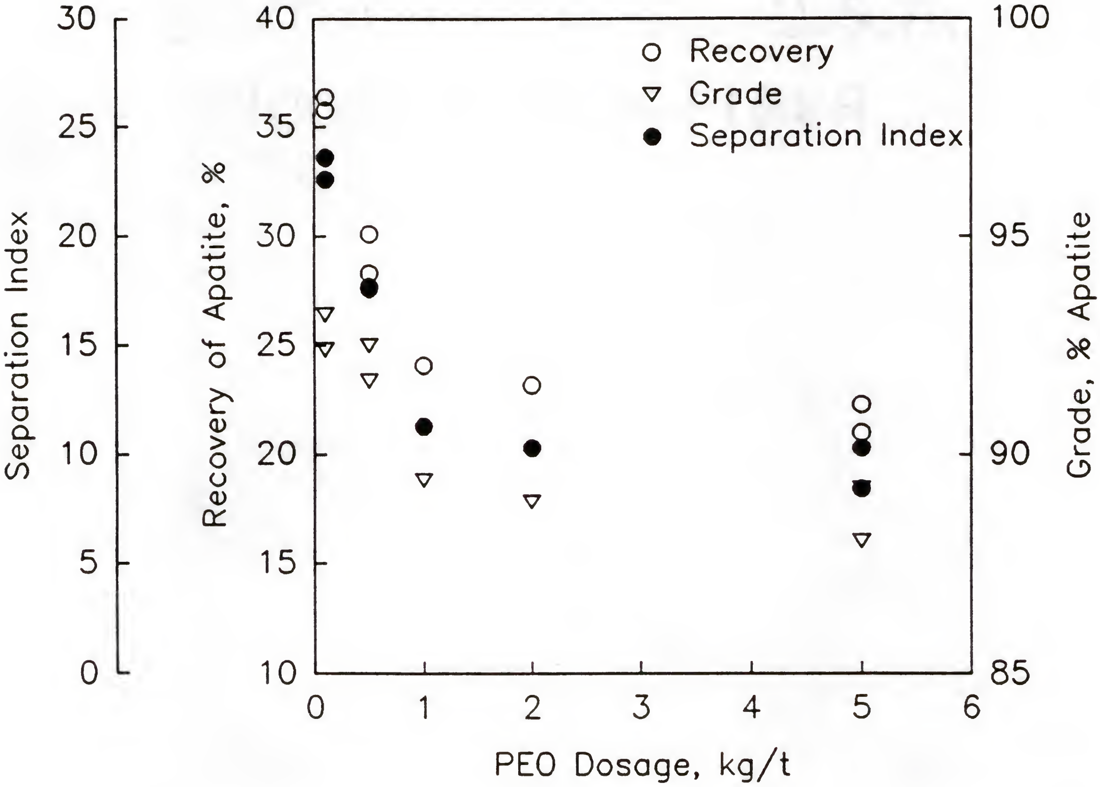


Figure 4.9: Mixed Mineral Flocculation Test Of A 80:20 Mixture Of Apatite And Dolomite.

Table 4.1: Effect Of Apatite/Dolomite Ratio On Flocculation.

Flocculant Dosage = 0.5 kg/t

Apatite in Feed, %	Grade, %	Recovery, % Apatite
50	83.2,84.6	43.3, 45.4
70	88.3,87.5	38.4, 39.7
80	93.2,92.4	35.8, 36.4

in all the cases that the recovery of apatite is small indicating a loss in selective floc formation.

Reasons for Loss in Selectivity

The loss in selectivity in a mixed mineral system has been attributed to a number of reasons such as heterocoagulation, ion activation, physical entrapment, entrainment and heteroflocculation. Shah's [Sha86] work on apatite-dolomite-PEO system showed that the loss in selectivity was mainly due to heteroflocculation. This was investigated by conducting adsorption tests under conditions identical to the flocculation tests. Adsorption results for 2 minute polymer contact time presented in Figure 4.10, indicate that a significant amount of PEO adsorbs on both apatite and dolomite, therefore, heteroflocculation can be expected. Considering that the particles are highly porous and the effective surface area for adsorption cannot be measured accurately, the adsorption density results are presented in terms of per unit weight of dry solids.

Control of Heteroflocculation

According to the predictive model by Moudgil and Behl [Mou91], loss in selectivity due to heteroflocculation can be overcome under two conditions. These are

1) using a flocculant which exhibits high adsorption selectivity
2) extremely low polymer dosages

Saturation adsorption results plotted in Figure 4.11 reveal that almost four times more PEO adsorbs on dolomite than apatite. The adsorption on apatite, under flocculation conditions, however, is enough to cause heteroflocculation (see Figure 4.10), therefore, it is clear that PEO adsorption is not selective enough to yield formation of only dolomite

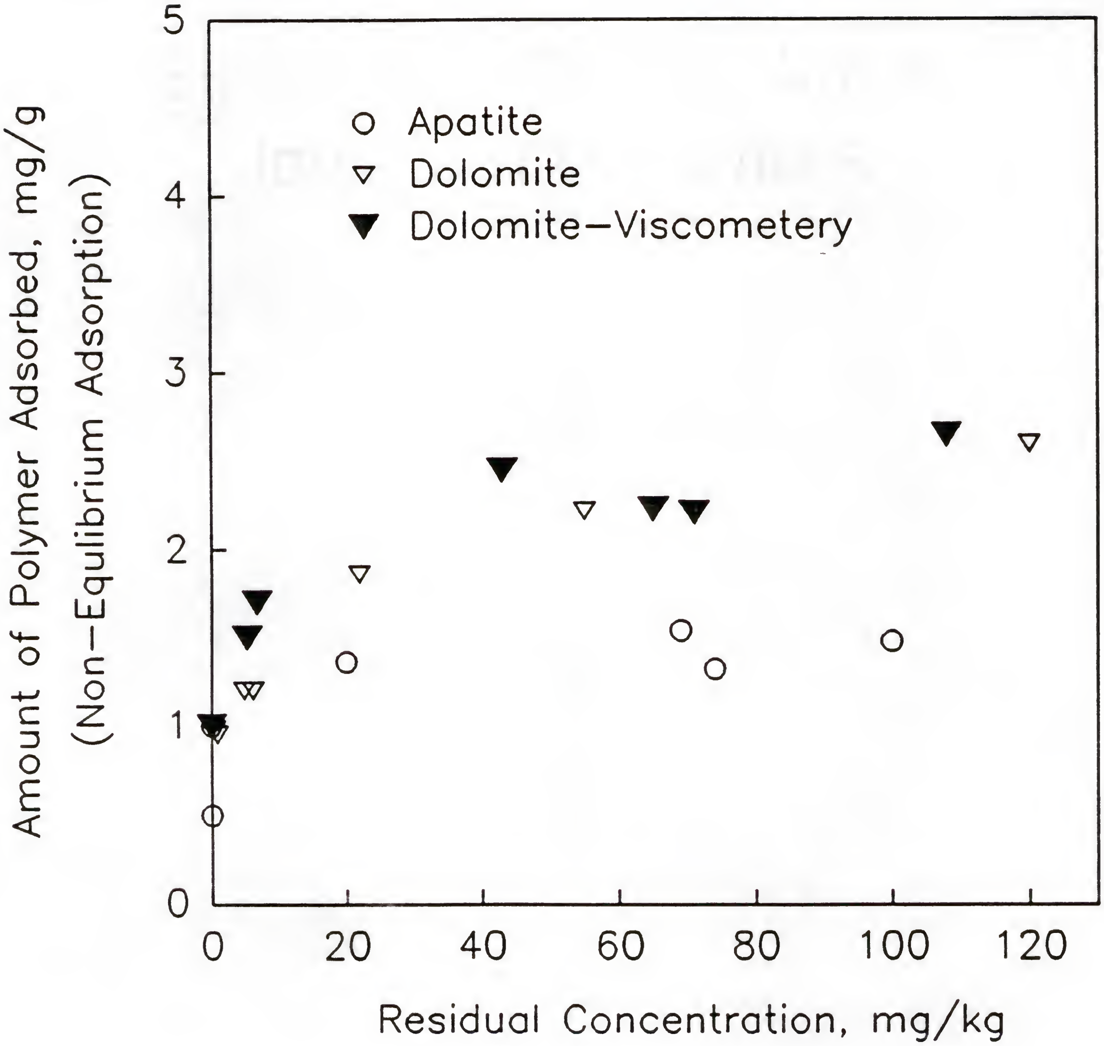


Figure 4.10: Non-Equilibrium Adsorption Of The Flocculant On Apatite And Dolomite.

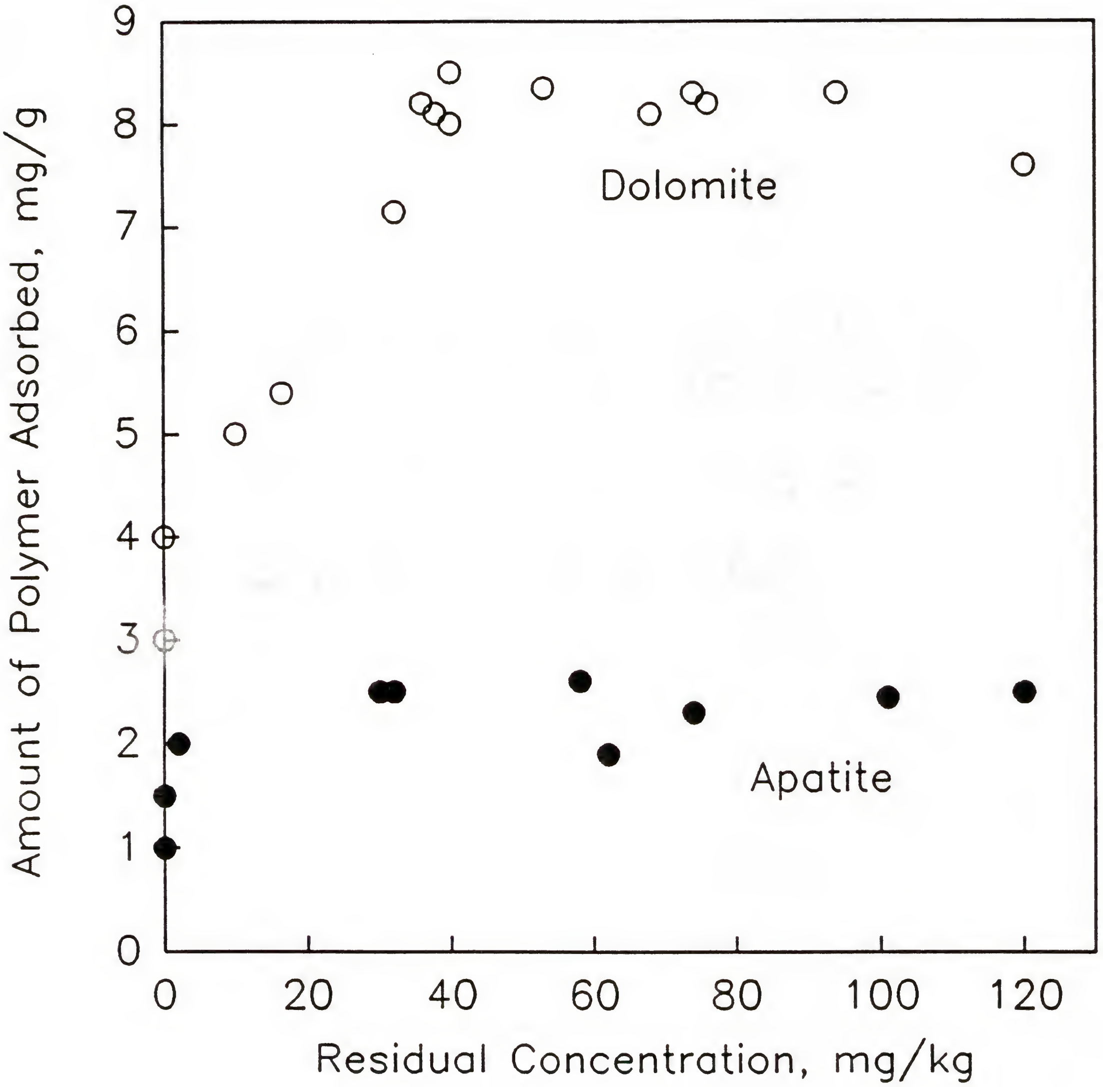


Figure 4.11: Equilibrium Adsorption Of PEO (Molecular Weight 5 X 10^6) On Apatite And Dolomite.

flocs. Regarding the effect of PEO dosage, it is observed from Figure 4.9 that only a slight increase in selectivity is achieved at low flocculant dosages. At this stage of the present study it was decided to evaluate the concept of site blocking agents to yield higher selectivity in flocculant adsorption.

An alternative method of either poisoning or blocking the surface sites using site blocking agents to enhance the selectivity in flocculant adsorption is suggested. Since the SBA itself should not be capable of flocculating itself for the purpose of preliminary experiments 100,000 molecular weight was selected. This is because flocculation in dolomite starts at 900,000 molecular weight (see Figure 4.8).

Results for the mixed mineral tests in the presence of the SBA are given in Table 4.2. It can be seen that a remarkable increase in the recovery of apatite is observed. This is because of decrease in the apatite-dolomite floc formation or heteroflocculation.

It can be seen that the concept of site blocking agent shows promise in controlling heteroflocculation. The rest of the study deals with rationalizing both experimentally and mathematically the concept for successful use of SBA to control heteroflocculation.

Table 4.2: Effect Of SBA On Selective Flocculation.

Flocculant PEO Molecular Weight 5 X 10^6

SBA PEO molecular Weight 1 X 10^5

Flocculant Dosage 1.0 kg/t

SBA Dosage, kg/t	Grade, %	Recovery, % Apatite
0	90.1	26.3
2	89.1	71.6

CHAPTER 5
CONTROL OF HETEROFLOCCULATION : A QUANTITATIVE MODEL

Introduction

Aggregation of polymer coated particles, as explained in Chapter 2 is governed by the frequency and efficiency of collisions of the particles. The polymer adsorption mechanism on different constituents of the mixture is considered to be similar, therefore, the probability of adhesion would be governed by collision efficiency between the flocculant coated and the bare sites on various particles and vice versa. A number of expressions suggested to explain floc formation have either overestimated or underestimated the collision efficiency factor except under certain specific conditions [Sme57, Hog84, Mou87c, Mou91] . In a model proposed recently by Moudgil et al. [Mou87c, Mou89b, Mou91], only those sites which are capable of interacting with a given polymer are considered to be "active" sites. It should be noted that the relative number of such sites would depend on the interaction of the polymer and the solid surface. The fraction of active sites and the effective surface coverage were estimated by saturation and non-equilibrium adsorption isotherms respectively [Sha86].

The expressions by Hogg [Hog84] and Moudgil et al. [Mou87c, Mou89b, Mou91] can account for heteroflocculation while the others are for bulk flocculation. However, the collision efficiency is overestimated by Hogg for any fraction of the surface coverage

(θ) except 0 and 1. This was attributed to the large number of sites on the surface to which the polymer molecule is attached. In other words , almost all the surface sites are implicitly considered to be capable of adsorbing polymer molecules. Moudgil's expression seems to correlate well with the selective flocculation data [Mou91]. In the limiting cases Moudgil's expression for collision efficiency given below reduces to the corrected version of the one suggested by Smellie and La Mer [Sme57].

$$E_{ij} = \Phi_i \Phi_j [\theta_i(1-\theta_j) + \theta_j(1-\theta_i)] \tag{5.1}$$

where

Φ_i, Φ_j = fraction of sites on i and j that are active for polymer adsorption

θ_i , θ_j = fractional surface coverage (of active sites) at a given polymer dosage.

It should be noted that flocculation may not be observed in a system, for small θ or Φ values which would lead to near zero E_{ij}. Further the collision efficiency is shown to be a strong function of Φ and is weakly related to θ [Mou91]. Also Moudgil and Behl [Mou91] proposed a critical efficiency factor (E_{ij}) and suggested that below the critical value of E_{ij}, no significant flocculation is observed.

Expression for Collision Efficiency in the Presence of SBA

To develop an expression for estimation of the collision efficiency for the particles in the presence of the site blocking agent (SBA), it is assumed that the lower molecular weight polymer (SBA) is introduced in the system prior to the injection of the flocculant. This would lead to adsorption of the SBA first and the flocculant would encounter a partially covered surface. The site on the surface can be defined as was done earlier by Hogg [Hog84] and Moudgil [Mou89b], to be the area occupied by the adsorbed polymer molecule. Floc formation would be observed if a coated site collides with the "active" bare site or vice versa. Any collision of a flocculant coated site with SBA coated site or vice versa will not yield flocculation. The implicit assumption of La Mer's model, that orientation of the particles,as well as the adsorbed polymer conformation remains unchanged as the particles approach one another, are maintained in this model. Although some reorientation due to flocculant-SBA, SBA-SBA , flocculant-flocculant, particle-flocculant, particle -SBA and particle-particle interactions, can not be ruled out, however, due to the small time scales involved in the collision process contribution of such reorientation may be minor. It appears to be more reasonable to assume that reorientation of the adsorbed polymer takes place once the particles have collided and bridging has been initiated, in which case the inter particle distances are smaller and the time available for reorientation longer.

Consider the number of sites for the SBA on the particle *i* to be n_i, of these a_i are active sites. Let the dosage be such that x_i sites are covered by the site blocking agent. Similarly for the flocculant, the total number of sites are N_i of which A_i are active and at a particular dosage X_i of these active sites are covered. Schematic representation of the area of polymer adsorption site on the surface is given in Figure 5.1. It can be seen from the figure that more area for active sites are available for the flocculant than for the SBA. The total number of sites on the surface for the SBA and the flocculant can, however, be related, since the available area is the same, by a factor which would depend on the respective parking areas of the molecules.

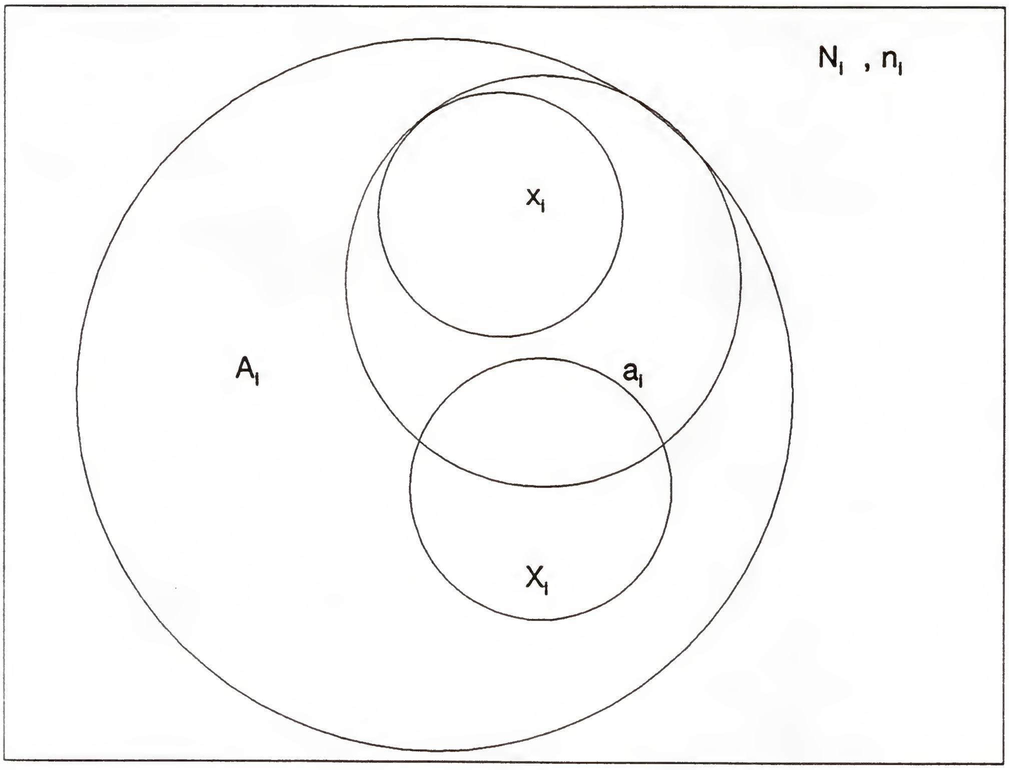


Figure 5.1: Schematic Representation Of The Solid Surface For Polymer Adsorption.

The probability of a given surface site on particle *i* being covered by polymer (flocculant) is given by the following expression

$$P_i = \frac{X_i}{N_i} = \frac{A_i}{N_i} \times \frac{X_i}{A_i} = \Phi_i \, \theta_i \tag{5.2}$$

where Φ_i is the fraction of the active sites and θ_i is the fractional surface coverage of the flocculant in the absence of the SBA.

To estimate the bare "active" sites on the particle, the number of sites available for the flocculant have to be estimated after the SBA adsorbs. This may be given by the expression,

$$A_j - \frac{x_j}{n_j} N_j \tag{5.3}$$

where

A_j = Number of Active sites on particle j.

x_j = Number of sites covered with the SBA on particle j.

n_j = Total number of sites for the SBA on particle j.

N_j = Total number of sites for the flocculant on the particle j.

The probability of a given site on a particle j being free of both SBA and the flocculant is

$$P_j = \frac{A_j - \frac{x_j}{n_j} N_j - X_j}{N_j} \tag{5.4}$$

and this can be shown to be

$$P_j = \Phi_j - \Phi_j\theta_j - \bar{\Phi}_j\bar{\theta}_j \tag{5.5}$$

where

$\bar{\Phi}_j$ = fraction of sites on j that are active for SBA adsorption

$\bar{\theta}_j$ = fractional surface coverage (of active sites for SBA adsorption) on *j* by the SBA at a given dosage.

The joint probability of collision of a covered active site on particle i with a bare active site on particle j is given by

$$P_iP_j = \Phi_i\theta_i[\Phi_j - \Phi_j\theta_j - \bar{\Phi}_j\bar{\theta}_j] \tag{5.6}$$

The collision efficiency factor is given by the overall probability of adhesion by considering the joint probability of particle i having a free active site and particle j a polymer coated patch. This can be expressed as

$$\bar{E}_{ij} = \Phi_i\Phi_j[\theta_i(1 - \theta_j) + \theta_j(1 - \theta_i)] - \Phi_i\bar{\Phi}_j\theta_i\bar{\theta}_j - \bar{\Phi}_i\Phi_j\bar{\theta}_i\theta_j \tag{5.7}$$

where $\bar{E}_{ij}$ is the collision efficiency in the presence of the SBA. It is clear from the above expression that in the absence of SBA the above equation reduces to the expression proposed by Moudgil et al. [Mou87c, Mou89b, Mou91].

In particular cases where all the particles have the same polymer coverage and the same fraction of the active sites, for example in a single mineral suspension, equation (5.7) reduces to

$$\bar{E} = 2\Phi^2\theta(1 - \theta) - 2\Phi\bar{\Phi}\theta\bar{\theta} \qquad (5.8)$$

which can be written as

$$\bar{E} = E - 2\Phi\bar{\Phi}\theta\bar{\theta} \qquad (5.9)$$

where E is the collision efficiency for single mineral particles.

Further if all the surface sites are considered to be active then the above expression reduces to

$$\bar{E} = 2\theta(1 - \theta - \bar{\Phi}\,\bar{\theta}) \qquad (5.10)$$

and if no SBA was present (i.e., $\bar{\Phi}\bar{\theta}$ =0) the equation (5.10) reduces to the equation suggested by Hogg as the corrected formulation of the La Mer model. To quantify the role of SBA in flocculation, equation (5.8) is considered for a single mineral and (5.7) for the mixed mineral case. The use of these equations is possible only after the values of the adsorption parameters (Φ, θ, $\bar{\Phi}$, $\bar{\Theta}$) are known.

Determination Of Adsorption Parameters

Estimation of fraction of active sites on a surface can pose some problems since direct measurements are not possible. However, if a certain surface, where high adsorption density and flocculation is observed, can be considered to be totally active, the value for Φ in such a case can be arbitrarily set at one, as was done for dolomite - PEO (5 million molecular weight) system by Moudgil et al. [Mou87c, Mou89b, Mou91]. Assuming the same size of active site on another surface, Φ for a given mineral may be determined with reference to the active surface, by the following expression.

$$\Phi = \frac{\Gamma_{max}}{\Gamma_{max}^{ref}} \tag{5.11}$$

where Γ_{max} is the saturation adsorption density for the two minerals.

The surface coverage (θ) may be estimated for a particular mineral by the expression

$$\theta = \frac{\Gamma}{\Gamma_{max}} \tag{5.12}$$

The surface coverage ($\bar{\Theta}$) by the SBA would be given by an expression similar to equation (5.12). However, $\bar{\Phi}$ has to be estimated by taking into account the difference in the size of the active sites for the SBA and the flocculant molecule. A general expression based on the definition for $\bar{\Phi}$ can be given as

$$\frac{\bar{\Phi}}{\Phi} = \frac{a}{n} x \frac{N}{A} \tag{5.13}$$

where 'a' and 'A' are the number of active sites for the SBA and the flocculant respectively. 'n' and 'N' are the corresponding number of total sites on the surface and Φ is the fraction of active sites for a reference material. Clearly, for a molecule with the same monomeric unit the size of the active site for a SBA would be smaller than the flocculant, therefore, the total number of sites for the flocculant are smaller in number.

In general the number of active sites on a particle surface for a given polymer is directly proportional to the equilibrium adsorption density expressed in terms of moles per unit area. Further the number of sites (both active or inert) are inversely related to the size of the polymer molecule (R_g). It is well known that the radius of gyration is related to the molecular weight of the polymer by the following expression [All81]

$$\langle R_g \rangle^2 \quad \alpha \quad M_w^{\frac{2}{3}(1+\gamma)} \tag{5.14}$$

where M_w is the molecular weight of the polymer and γ is intrinsic viscosity parameter. An expression for the fraction of active sites for a SBA using the above argument can be given as

$$\frac{\bar{\Phi}}{\Phi} = \left(\frac{\bar{\Gamma}_{max}}{\Gamma_{max}}\right) x \left(\frac{m}{M}\right)^{\frac{2\gamma - 1}{3}} \tag{5.15}$$

where Γ_{max} and $\bar{\Gamma}_{max}$ are the saturation adsorption densities (g/unit area) for the reference (high molecular weight polymer with $\Phi = 1$) and the SBA molecule. It should be noted that the saturation adsorption for the lower molecular weight fraction is smaller than the higher molecular weight macromolecules [Coh82, Bla90], therefore, $\bar{\Phi}$ is less than one.

Single Mineral Flocculation

It is clear from equation (5.8) that in the presence of SBA the collision efficiency would be lower. This decrease would of course depend on the product of $\bar{\Phi}$ and $\bar{\Theta}$ (termed as SBA adsorption parameters). Physically the former term signifies the type of SBA used while the latter denotes the dosage employed. A higher $\bar{\Phi}$ would be expected for a larger molecular weight SBA molecule which clearly should have better site blocking capabilities. Since the fraction of active surface for a flocculant is much larger than that for the SBA, it would not be possible to depress flocculation of the active component ($\Phi = 1$).

It is clear from Figure 5.2 that for material with $\Phi = 1$ the surface coverage (θ_{max}) for maximum E would decrease from 0.5 for no SBA to about 0.25 if the SBA adsorption parameter is 0.5. However, if $\Phi = 0.5$ then on increasing the SBA adsorption parameter the θ_{max} reduces from 0.5 to zero, implying SBA would strongly depress flocculation if the material itself exhibits low tendency towards floc formation. This can be observed from the decrease in the absolute value of E for cases with Φ less than one (see Figure 5.3). Moudgil et al. [Mou89b], Shah [Sha86] and Hogg [Hog84] have shown that the collision efficiency factor is directly related to the amount of flocculation. Therefore, flocculation is difficult to suppress in cases with $\Phi = 1$ as the SBA adsorption parameter value of 1.0 is not practical. However, in cases where the Φ is 0.5, which implies using a weaker flocculant molecule, depression of flocculation is easily achievable with SBA.

Coverage For Maximum Flocculation

The dosage required to obtain maximum flocculation in single minerals can be calculated from the proposed expression [Sme57, Hog84, Mou87c]. It can be easily shown that maximum flocculation would be observed at half surface coverage. This, however, was not found to be true in a number of systems studied latter [Sme57, Lin59, LaM63, Sin73, Hog84, Mab84, Som84].

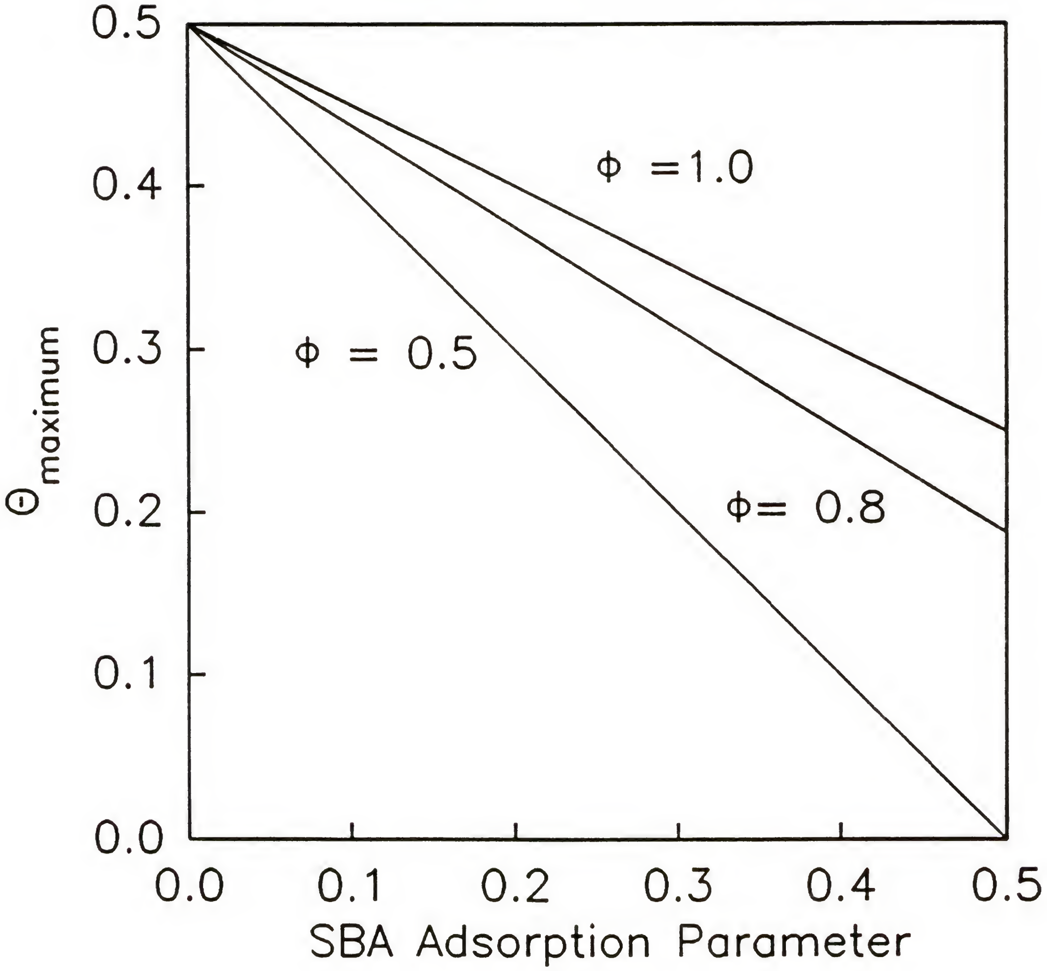


Figure 5.2: Effect of SBA Adsorption Parameter On The Surface Coverage (θ_{max}) For Maximum Collision Efficiency.

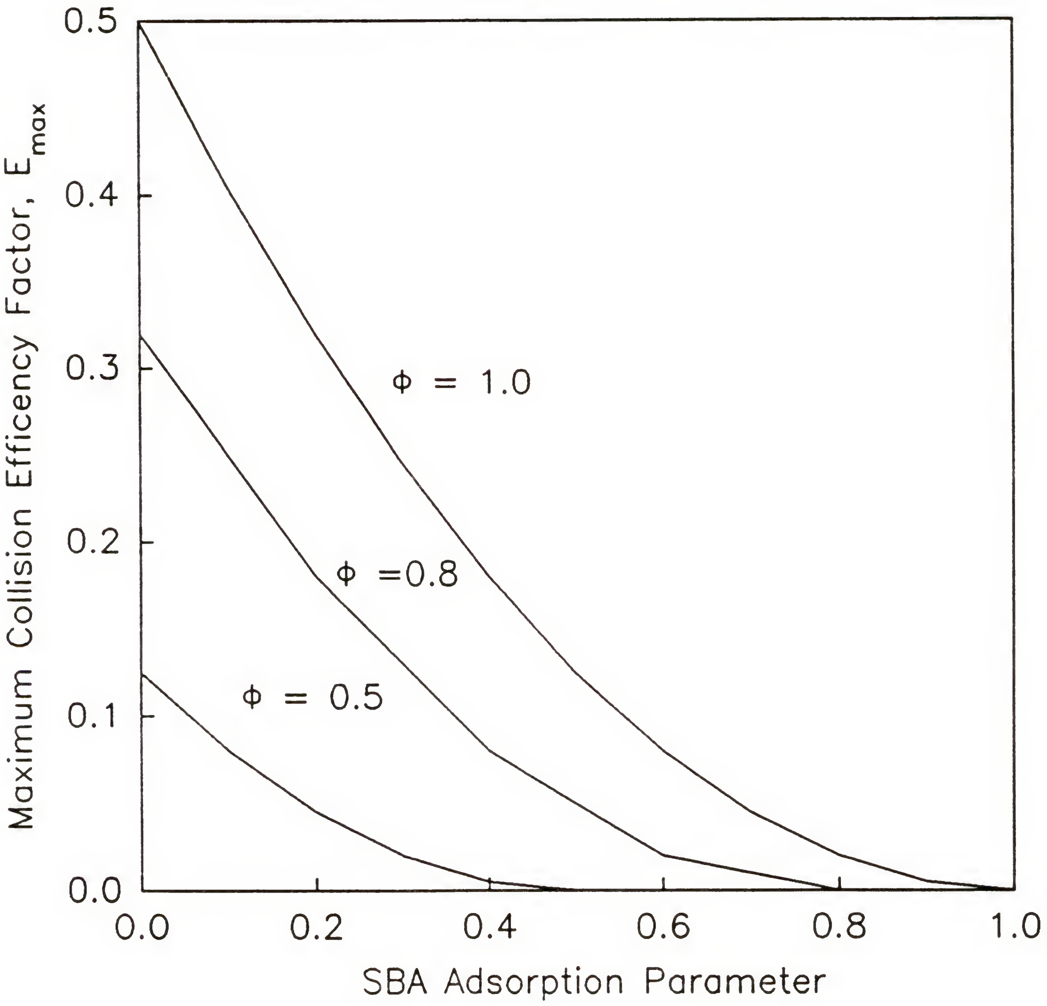


Figure 5.3: Effect of SBA Adsorption Parameter On The Maximum Collision Efficiency Factor (E_{max})

In the presence of a SBA the surface coverage corresponding to maximum in flocculation (θ_{max}) can be obtained by simply maximizing θ in the equation (5.8) and is given by the expression

$$\theta_{max} = (\frac{\Phi - \bar{\Phi}\,\bar{\theta}}{2\Phi}) \tag{5.16}$$

The maximum value of collision efficiency can be obtained by substituting θ_{max} in the equation (5.8)

$$\bar{E}_{max} = \frac{1}{2}(\Phi - \bar{\Phi}\,\bar{\theta})^2 \tag{5.17}$$

The above expression reduces to the limiting cases of Smellie and LaMer's model and Hogg's expression ($\theta_{max} = 1/2$) when the SBA is absent and the entire surface is considered active. It can be seen from Figure 5.4., case A, that in the absence of the SBA, maximum E is obtained at half the surface coverage. However, in the presence of the SBA, depending on the adsorption parameters ($\bar{\Phi}\bar{\theta}$), the maximum E would be obtained at a value lower than 0.5. For example, at $\bar{\Phi}\bar{\theta}=0.5$ (case D) maximum flocculation or collision efficiency factor (value of 0.125) would be obtained at a surface coverage of 0.25.

Most polymers have a wide molecular weight distribution, where the lower molecular weight fraction may not be capable of bridging. Further the smaller molecular weight fraction can adsorb faster than the bulky molecule and to a large extent can act like SBA. This may in part explain the observation of Hogg [Hog84] , Somasundaran et al. [Som84], Singer et al. [Sin73], Link and Booth [Lin59] that the maximum flocculation

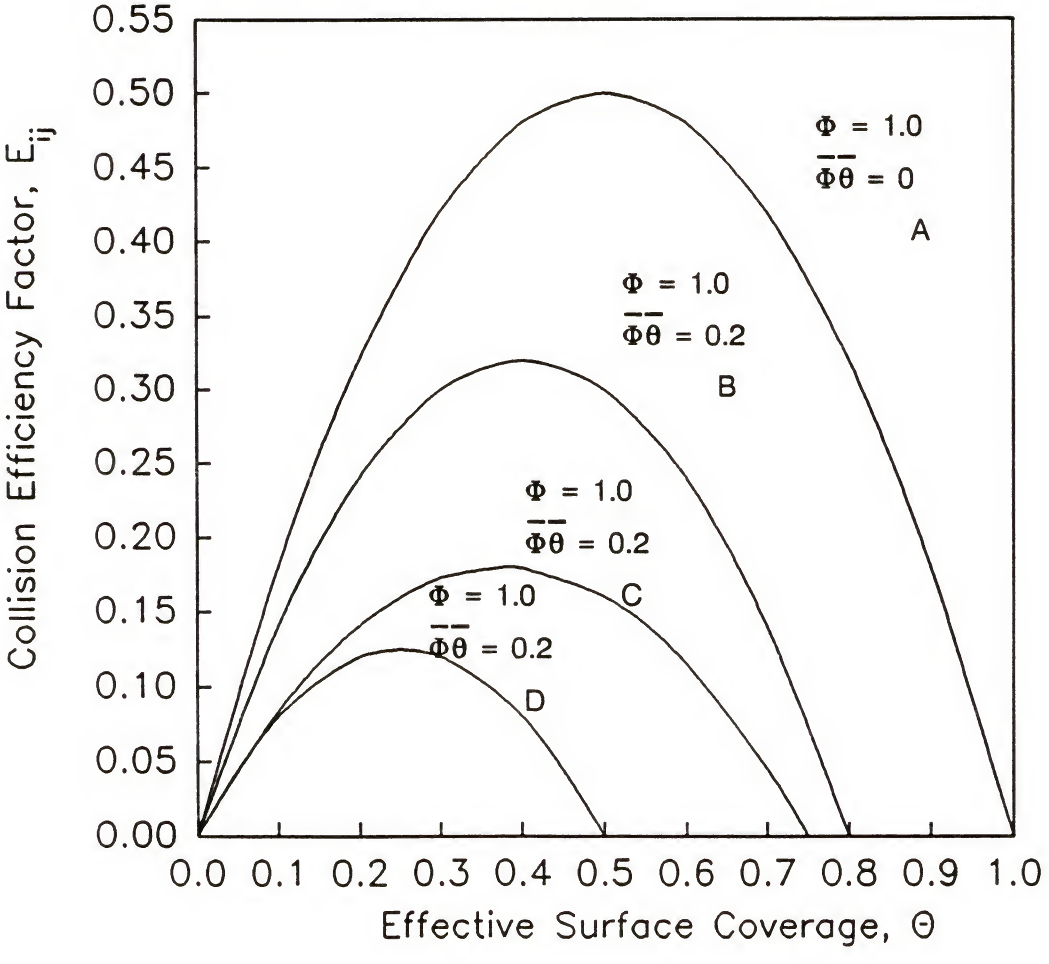


Figure 5.4: Effect of Effective Surface Coverage On The Collision Efficiency Factor (E_{ij}).

was obtained at a value slightly lower than the theoretically predicted value of 0.5. In fact Somasundaran and coworkers [Som84] observed a complete dispersion at half the surface coverage. This situation may correspond to Case D in Figure 5.4.

Mixed Mineral Flocculation

It is clear from equation (5.8) that the collision efficiency factor for mixed components in the presence of the SBA would decrease. If single mineral selectivity is observed then the E_{ij} is typically small (at least an order or two smaller than E for the active component), therefore, the decrease in this value would reduce heteroflocculation. A higher molecular weight SBA would be more efficient in reducing heteroflocculation, as it has a larger $\bar{\Phi}$ value.

In this chapter, it has been shown quantitatively that SBA would reduce heteroflocculation. In the next chapter results for control of heteroflocculation for apatite-dolomite -PEO system are illustrated.

CHAPTER 6
RESULTS AND DISCUSSION

Introduction

The concept of site blocking for separation of dolomite from apatite by selective flocculation is illustrated in this chapter.

Selection Of The Site Blocking Agents

The main characteristics of the site blocking agent(SBA) is its capability in blocking enough sites on the inert particles so as to minimize heteroflocculation. Clearly, to satisfy such a condition the adsorption mechanism for the flocculant and the SBA should be similar, if not the same. Also, it should not cause flocculation by itself. The ideal SBA molecule would, therefore, be the lower molecular weight fraction of the flocculant itself.

To select the SBA molecular weight, flocculation of dolomite was attempted with PEO of different molecular weight. It was seen earlier in Figure 4.8 that flocculation starts at molecular weight of 900,000, thereby imposing, an upper limit on the molecular weight of the polymer to be used as a SBA.

Single Mineral Tests

Flocculation Tests

Apatite did not exhibit flocculation with or without the SBA. In case of dolomite, a decrease in flocculation was observed with an increase in dosage or the molecular weight of the SBA (see Figure 6.1) as expected. The apatite surface may also be expected to be blocked significantly at a lower dosage of the SBA, as it has less number of sites as compared to dolomite. The effect of SBA adsorption on flocculation of dolomite, with PEO of 5 million molecular weight as a flocculant can be seen from Figure 6.2. Flocculation is depressed until a polymer (SBA) molecular weight of 600,000. As observed earlier, polymer molecules of higher molecular weight, are capable of flocculation (see Figure 4.8). Also the total amount of polymer capable of adsorbing on dolomite increases with molecular weight, thereby exhibiting better capabilities for blocking the sites (See Figure 6.2).

In order to understand the mechanism underlying the SBA effect, the adsorption behavior of lower molecular weight PEO/PEG (molecular weights up to 600,000) on apatite and dolomite was determined. PEG of molecular weight less than 1000 was not considered since these molecules act more as surfactants and their adsorption behavior is known to be different from that of the polymers.

Adsorption Of PEO On Apatite And Dolomite

Dolomite and apatite used in this study are both porous, therefore, the available surface area for different molecular weight polymers may vary. This is because the size

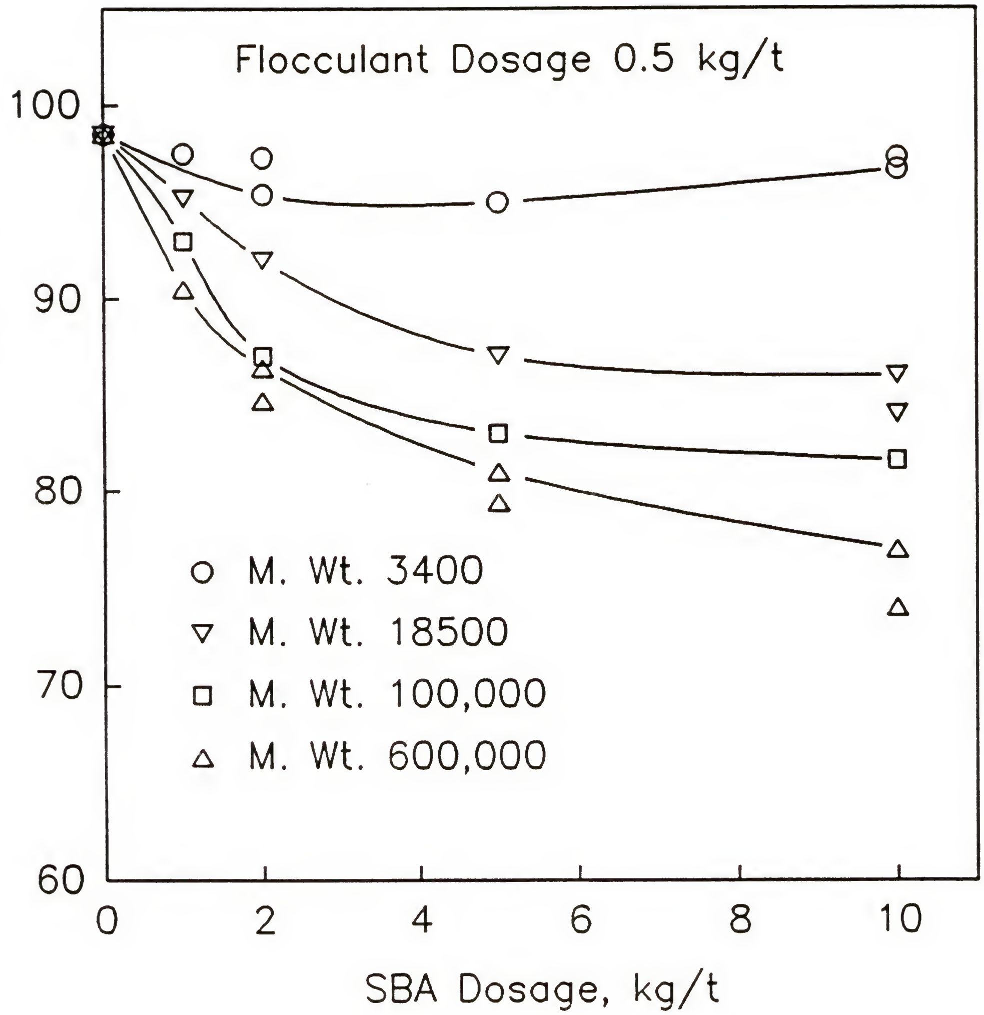


Figure 6.1: Effect Of Site Blocking Agent (SBA) On Dolomite Flocculation With PEO.

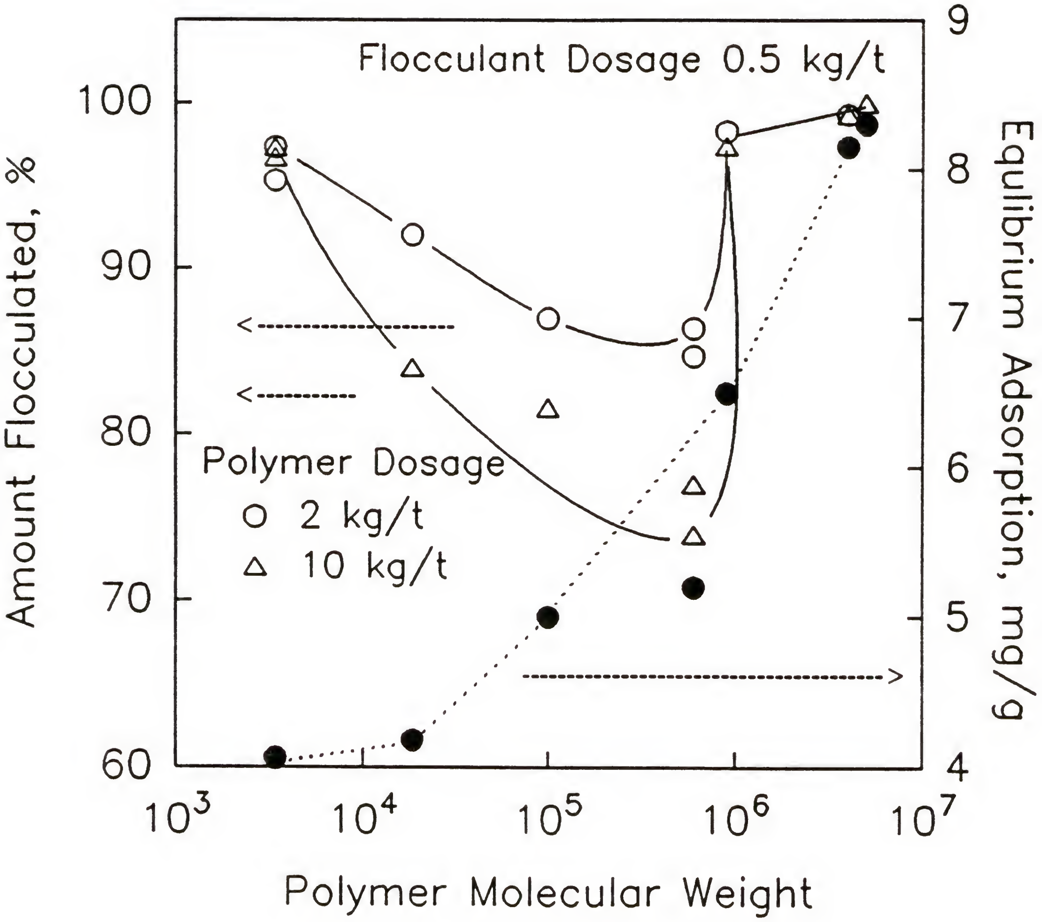


Figure 6.2: Effect Of SBA Molecular Weight On Dolomite Flocculation.

of the polymer molecule is a function of the molecular weight and the smaller molecules may adsorb inside the pores.

There are at present no methods available to measure the available surface area for adsorption of polymer molecules. The effective surface area, at best, can be estimated using the data from BET method. The adsorption density, therefore, for qualitative understanding the role of SBA, is reported in terms of weight of the solids. However, for quantifying the adsorption, estimated surface area is used and will be discussed latter in the chapter.

Adsorption of lower molecular weight PEO on dolomite

The non-equilibrium (contact time 7 minutes) adsorption isotherms of SBA (molecular weights 3400; 18500; 100,000; 600,000) are given in the Figure 6.3. The adsorption isotherms, as expected, are of high affinity type. Adsorption densities are larger for higher molecular weight suggesting increased effectiveness of molecules in blocking the sites for flocculant adsorption.

Equilibrium adsorption isotherms for the SBA molecules on dolomite are plotted in Figure 6.4. Similar characteristics as those of the non-equilibrium isotherms are observed.

It should be noted that more scatter is observed in the non-equilibrium as compared to the equilibrium adsorption isotherms. This may be attributed to the small time scale involved in the non-equilibrium adsorption measurements.

Adsorption of lower molecular weight PEO on apatite

Non-equilibrium and equilibrium adsorption isotherms of PEO on apatite show the same features as that on dolomite (Figures 6.5 and 6.6). Total adsorption of the SBA on apatite is much lower than on dolomite. However, at a dosage of 0.5 kg/t all the polymer

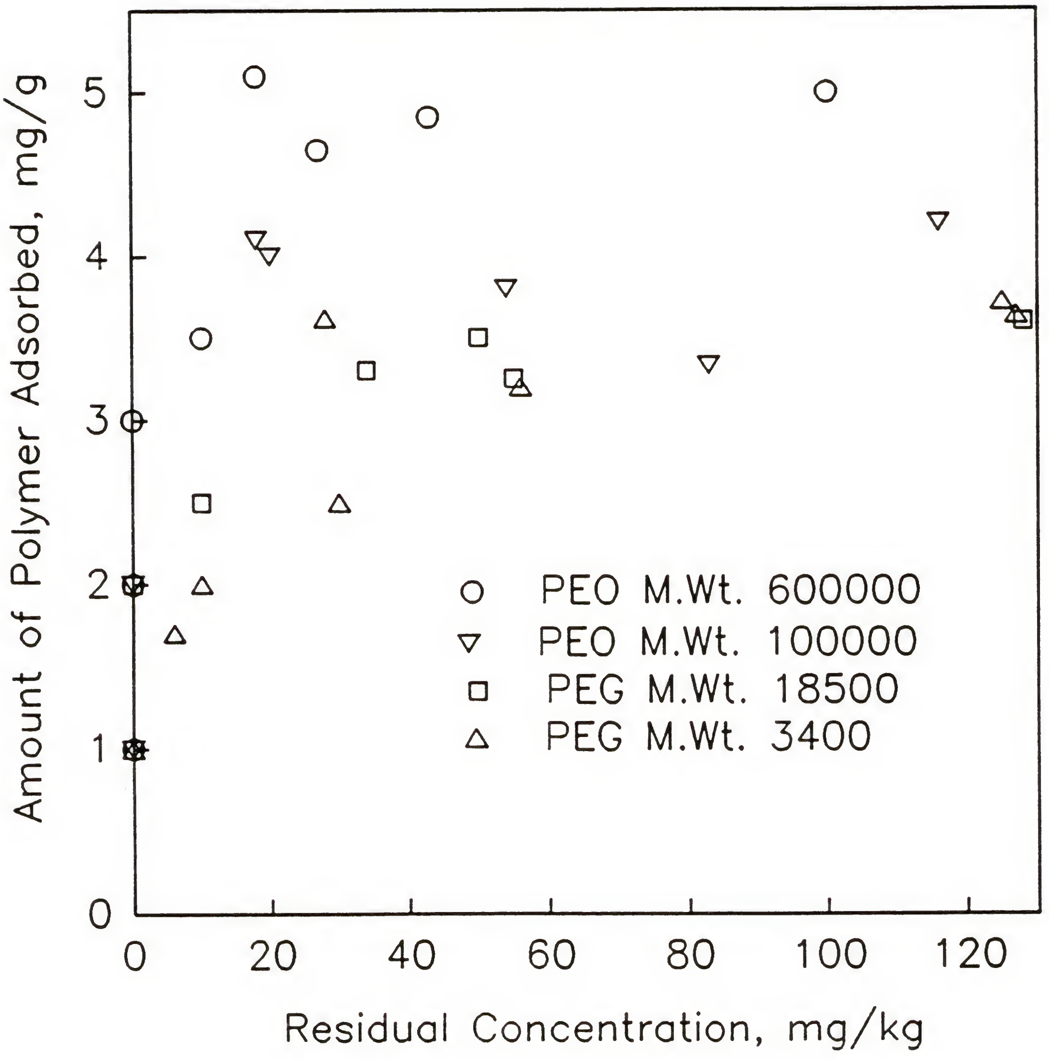


Figure 6.3: Non-Equilibrium Adsorption Of Site Blocking Agent On Dolomite.

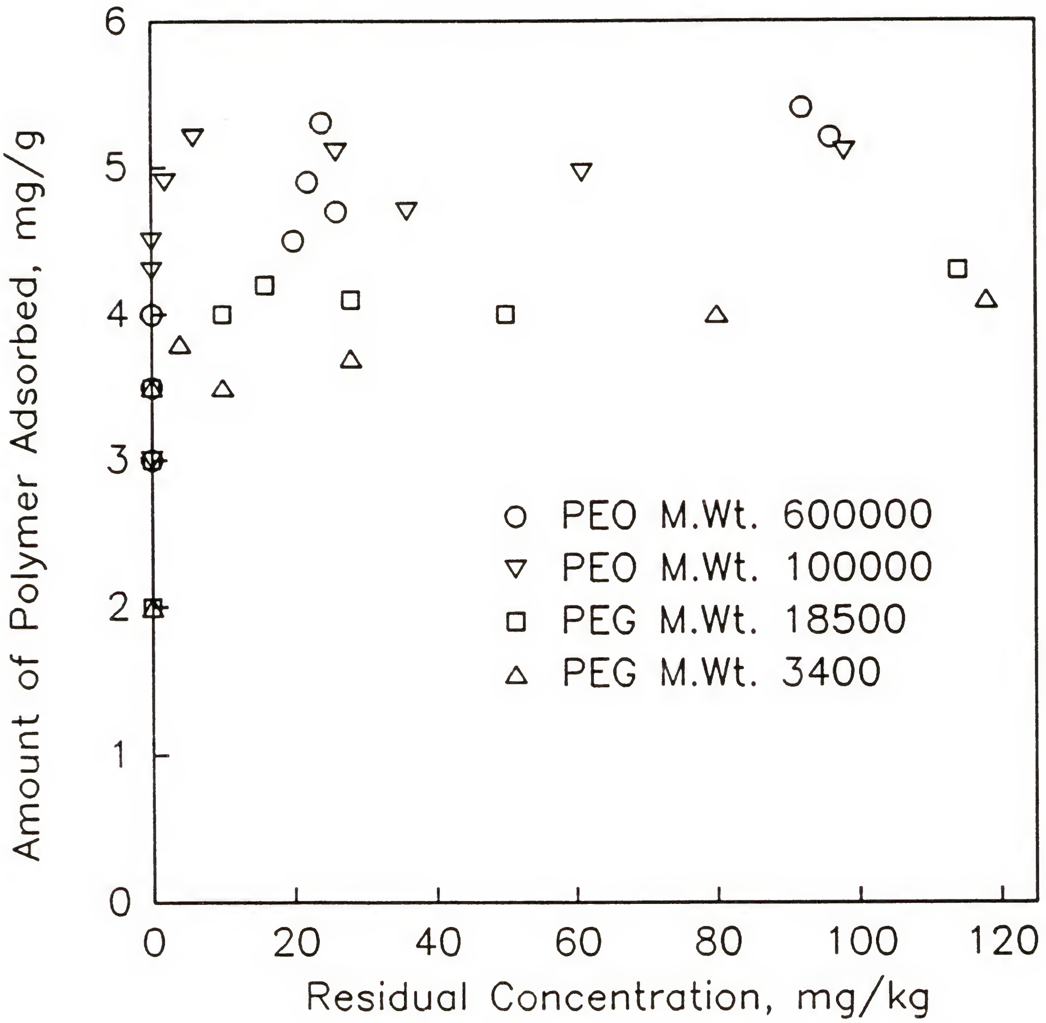


Figure 6.4: Equilibrium Adsorption Of Site Blocking Agent On Dolomite.

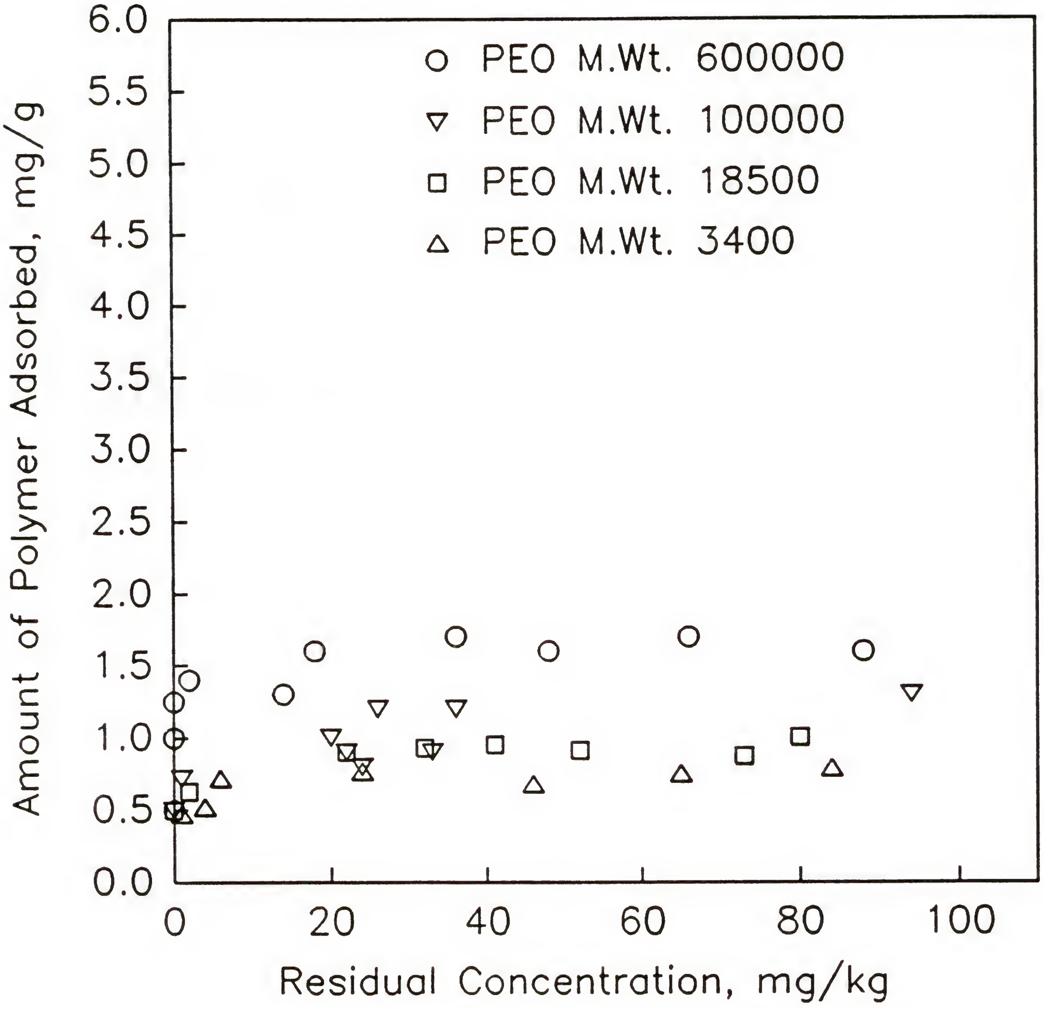


Figure 6.5: Non-Equilibrium Adsorption Of Site Blocking Agent On Apatite.

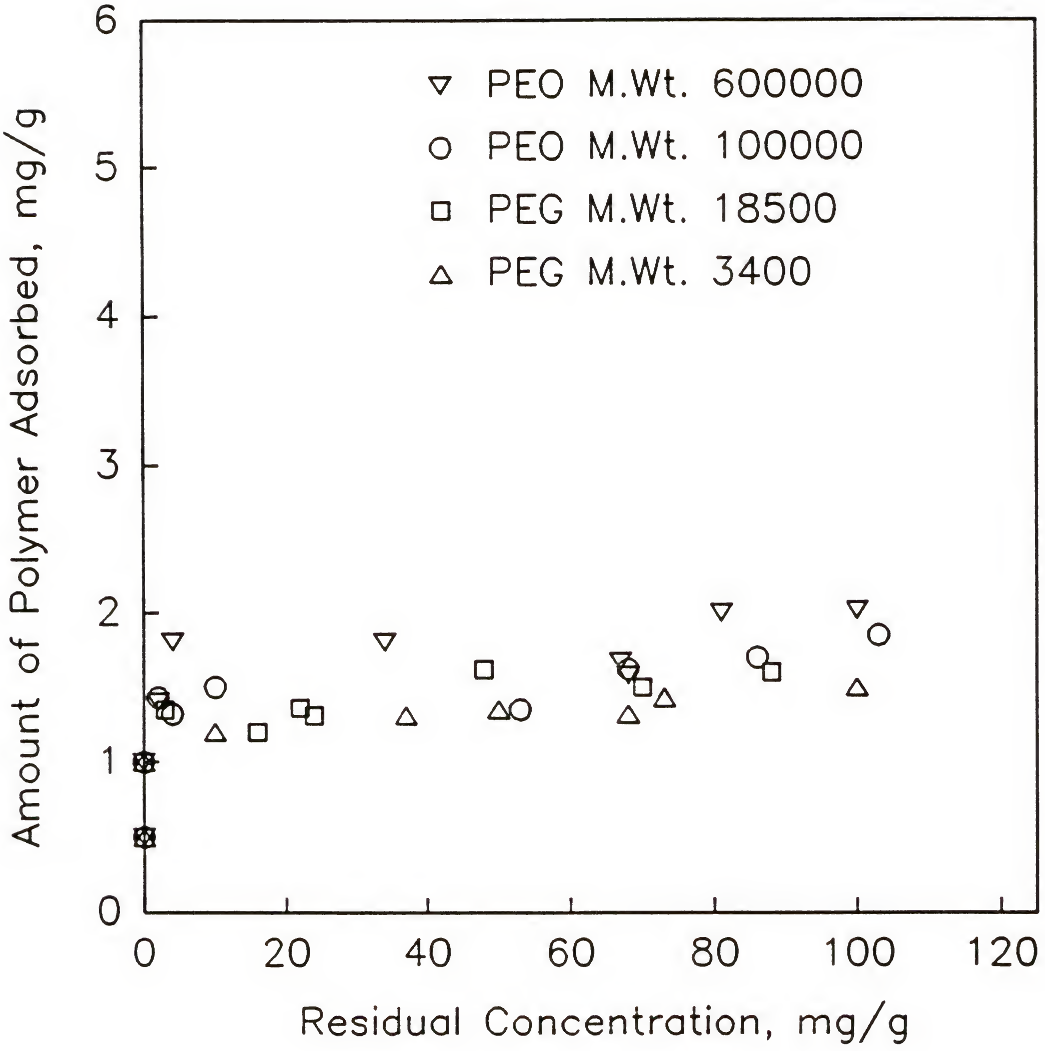


Figure 6.6: Equilibrium Adsorption Of Site Blocking Agent On Apatite.

adsorbs on both the apatite and dolomite surfaces. Therefore, the use of low SBA dosage may be superior for effectively blocking the sites on the apatite surface, since at higher dosages the residual polymer may adsorb also on dolomite surface. This would make the molecular weight of the SBA a more important parameter than the dosage for effective site blocking.

The saturation adsorption on apatite is significantly smaller than on dolomite (see Figure 6.7). Also, it should be noted that no significant difference in the equilibrium and non-equilibrium adsorption isotherms is observed. This implies that the contact time of the polymers with the solids would not significantly affect the efficiency of the SBA.

Clearly the highest molecular weight fraction of the flocculant itself which is not capable of flocculation (600,000 in the present case) can be considered to be the most efficient site blocking agent. The mixed mineral tests using 600,000 molecular weight PEO as SBA are discussed next.

Mixed Mineral Tests : Flocculation

Mixed mineral flocculation of a 80:20 mixture of apatite and dolomite was attempted at two flocculant concentrations for various SBA (molecular weight 600,000) dosages. It can be seen from Figure 6.8, that at a given flocculant dosage, increasing the SBA concentration results in higher recovery of apatite, thereby, indicating less heteroflocculation. Further on increasing the flocculant dosage, a higher loss in selectivity is observed. The best separation efficiency as shown in Figure 6.9 is obtained for a SBA dosage of 2 kg/t. At higher SBA concentrations significant loss in dolomite flocculation is expected, thereby lowering the grade of the concentrate. It should be realized that separation efficiency is a stronger function of the grade of the concentrate

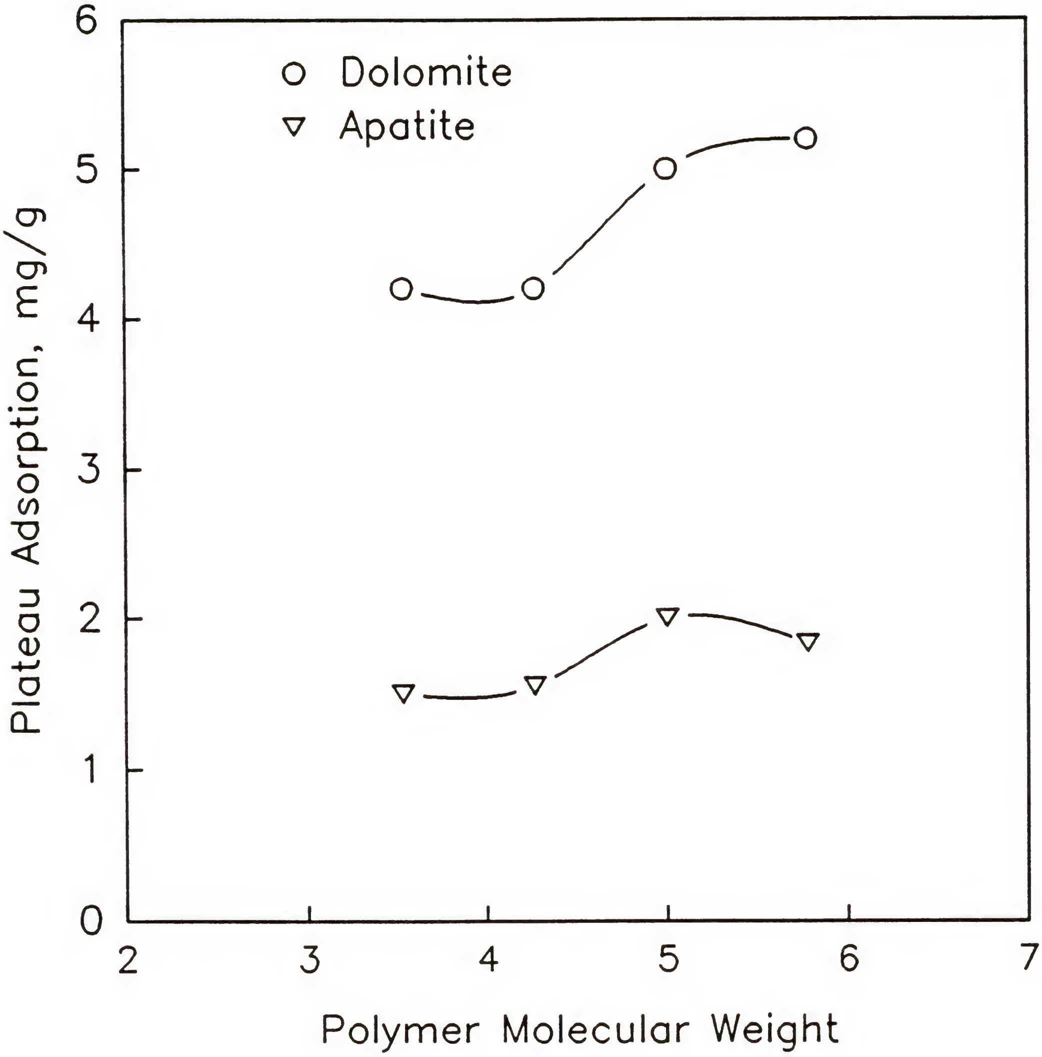


Figure 6.7: Plateau Adsorption Of Site Blocking Agent On Apatite And Dolomite.

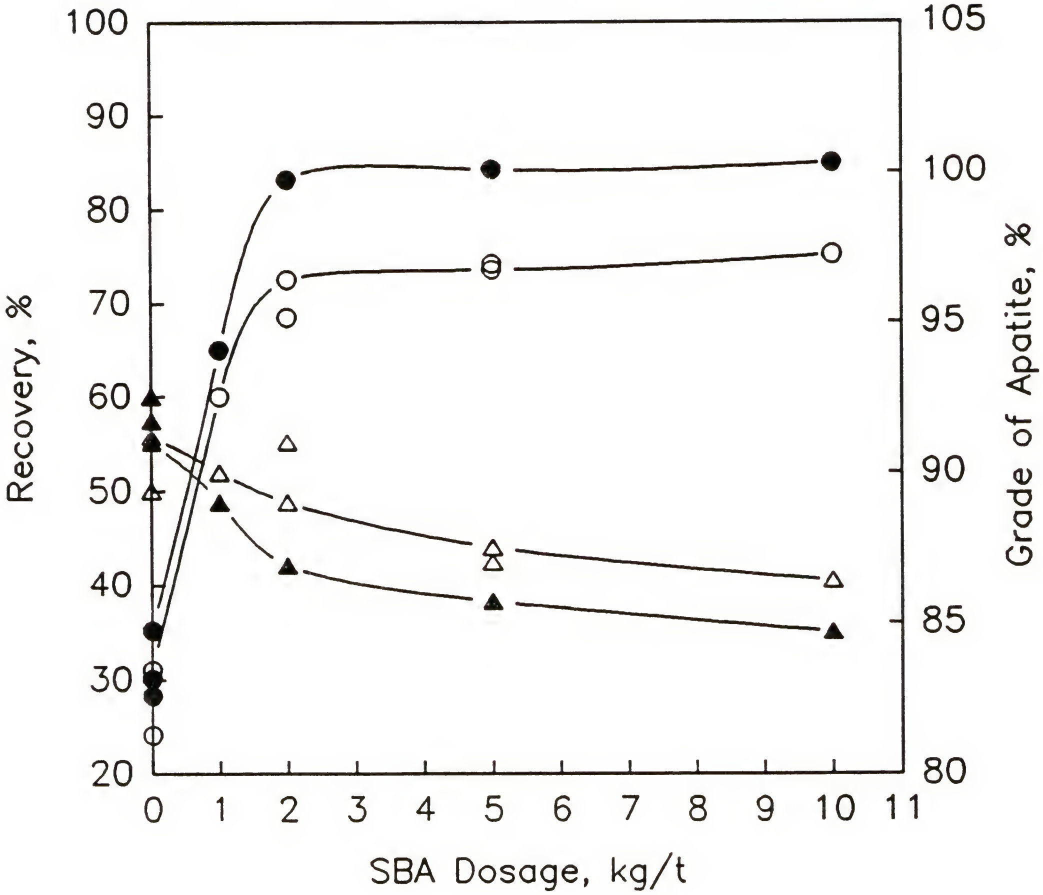


Figure 6.8: Mixed Mineral Flocculation Of 80:20 Mixture Of Apatite And Dolomite Using SBA.

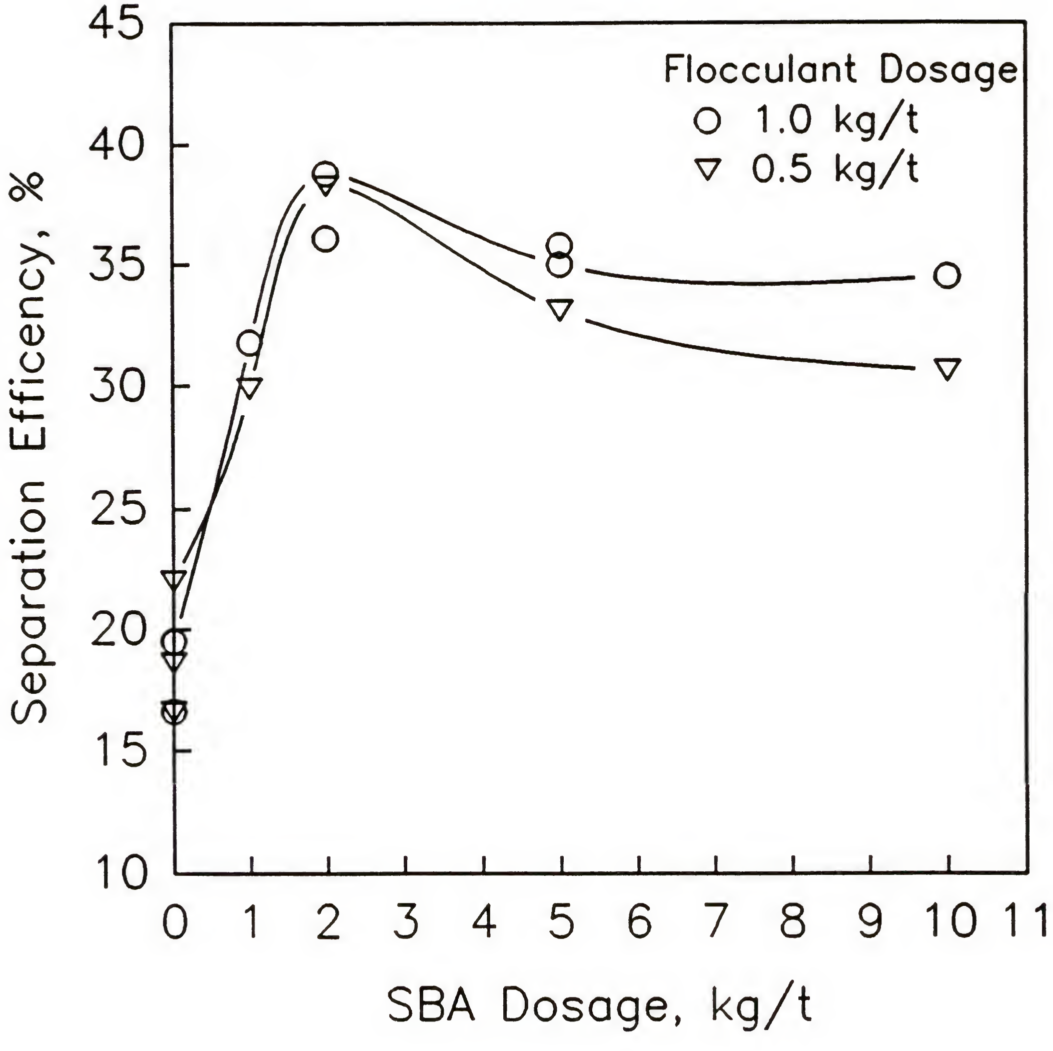


Figure 6.9: Separation Efficiency AS A Function Of The SBA Dosage.

as compared to the recovery, therefore, the observed decrease in separation efficiency at higher SBA dosages is expected.

It is clear from the above results that heteroflocculation can be controlled by using a SBA. This can be attributed to the availability of less sites on apatite for flocculant adsorption after treatment with the SBA. This was confirmed by flocculant adsorption studies in the presence of the SBA.

Adsorption Of The Flocculant In The Presence Of SBA

A significant decrease in adsorption of the flocculant was observed in the presence of the SBA (Table 6.1). For example, at a flocculant dosage of 1 kg/t, all the flocculant adsorbed on both apatite and dolomite particles, but in the presence of 2 kg/t of SBA, the flocculant adsorption reduced to 0.1 kg/t on apatite and 0.66 kg/t on dolomite. Desorption of the SBA was assumed to be absent, as water is a bad solvent for higher molecular weight PEO, thereby making the process thermodynamically unfavorable. Further it is well known that the kinetics of polymers desorption from solid surfaces is very slow, of the order of days, therefore, by contacting the SBA coated particles with the flocculant for 2 minutes greatly reduces the chances for replacement of the smaller molecule on the surface with higher molecular weight PEO molecules. This is in agreement with literature reports on desorption of the higher molecular weight polymer molecules [Coh82, Coh84, Cos87, Ate88a, Ate88b].

Quantitative Explanation Of Selective Flocculation Process

Dolomite and apatite used in this study are porous, therefore, the available surface area for adsorption of different molecular weight polymers may vary. At present, no

Table 6.1: Adsorption Of The Flocculant On Apatite And Dolomite In The Presence Of SBA.

Flocculant Dosage = 1.0 mg/g

SBA Dosage mg/g	Adsorption, mg/g			
	SBA		Flocculant	
	Apatite	Dolomite	Apatite	Dolomite
1.0*	0.70	0.97	-	-
2.0*	1.26	1.93	-	-
0	-	-	1.00	1.0
1.0	0.70	0.97	0.97	0.61
2.0	1.26	1.93	0.10	0.66

* No Flocculant (only SBA)

methods which accurately measures the surface area for adsorption of polymer molecules is available. The effective surface area, at best, can be estimated using the data from BET method. The adsorption density, therefore, was earlier reported in terms of weight of the solids. Estimation of the effective surface area, however, is required for comparing adsorption on samples of different porosity and is discussed next.

Estimation Of The Effective Surface Area

It should be noted that the effective surface area for adsorption of the polymer molecules would be different from the geometric surface area since smaller molecules (smaller radius of gyration) can adsorb in pores. However, the size of the adsorbing polymer molecule is a strong function of the molecular weight, therefore, it is difficult to estimate the effective surface area for adsorption on a porous particle. In general, for most systems as described by Perkel and Ullman [Per61] polymers adsorb with a random coil conformation, unless there is specific interaction between the polymer molecule and the surface. According to these investigators, the polymer is believed to adsorb as a set of contiguous spheres proportional to the radius of gyration. The adsorption of a polymer molecule, however, may not be directly related to its radius of gyration, for example, in the case of adsorption due to single-point attachment on the surface. The conformation of the polymer in solution is required to explain its behavior on the solid surface. In solution, according to a theoretical approach [Tro83], the short chain molecules behave like small rods and the larger molecules as coils. The conformation in solution, may be evaluated by estimating the degree of coiling of a molecule, given by the ratio of L_{max} (the fully extended length) to the radius of gyration (R_g). The larger is the degree of coiling, the more coiled is the polymer. The extended length of a PEO molecule can be calculated by the product of the length of a monomer (0.36 nm) and the degree of polymerization (number of monomers). The radius of gyration of the molecule on the other hand, is determined by intrinsic viscosity data published earlier by Bailey and Koleske [Bai76]. The equations governing the intrinsic viscosity of PEO (in the molecular weight range 10^4-10^7) is given as follows.

$$[\eta] = 1.25 \text{ X } 10^{-4} M^{0.78} \tag{6.1}$$

where $[\eta]$ is the intrinsic viscosity in dl/g and M is the molecular weight. The intrinsic viscosity of PEG of molecular weight 3400, using the data published by Bailey and Koleske [Bai76] was found to be 0.07 dl/g. The radius of gyration was estimated using the Flory-Huggens equation

$$\bar{R}_g^{\,2} = \left(\frac{[\eta]M}{\phi}\right)^{\frac{2}{3}} = \left(\frac{K\ M^{1+\gamma}}{\phi}\right)^{\frac{2}{3}} \tag{6.2}$$

where Φ is the Flory-Huggens constant; and K and γ are constants from the intrinsic viscosity term. The degree of coiling for PEO of various molecular weights is given in Table 6.2, and it increases from 10 for 3400 molecular weight to 241 for a molecule of 5 million molecular weight. The five million molecular weight PEO is believed to have a random coil conformation [Tro83].

In the case of porous particles, the higher molecular weight polymer molecules may not be capable of diffusing into the pores and thus stay excluded from the micro-pores, implying that the BET surface area is a gross overestimation of the effective surface area for polymer adsorption. In cases of pore exclusion of the polymer molecules, Spaltro et al. [Spa92] have observed a maximum in the isotherm unlike the

Table 6.2: Degree of Coiling of PEO Molecules.

Polymer Molecular Weight	Degree of Coiling
5.00×10^6	241
4.00×10^6	218
9.00×10^5	120
6.00×10^5	102
1.00×10^5	49
1.85×10^4	25
3.40×10^3	10

high affinity type adsorption for most polymers. A proper accounting for the exclusion effect could reduce the deviant adsorption behavior to the expected trend of a saturation adsorption with increase in the polymer concentration [Spa92]. In the present system, no maximum was observed in the adsorption isotherms for any of the polymer molecular weights, in spite of significant porosity of the samples (See Figures 4.11, 6.4, 6.6). Adsorption on a porous particle, according to Howard and McConnel [How67a, How67b, How67c] is expected to decrease as the molecular weight of the polymer increases, which also was not observed in the present system. This would imply, that in the molecular weight range examined, the effective area for adsorption is the same for the higher and lower molecular weight polymers. The effective surface area is taken as the one corresponding to the pore which excludes a polymer molecule of a particular size. It has been shown that pores corresponding to the hydrodynamic radius of the polymer are excluded [Spa92]. The hydrodynamic radius is estimated by the following expression [Spa92];

$$R_h = 2\sqrt{6}R_g \tag{6.3}$$

where r_h and r_g are the hydrodynamic radius and radius of gyration respectively.

It should be noted that the estimation of the surface area based on the pore size corresponding to the lowest molecular weight polymer would overestimate "effective area" for higher molecular weight polymer adsorption hence underestimating the adsorption density of larger molecules. This assumption, however, would give conservative predictions of the floc formation process. Accordingly, the effective surface area for dolomite and apatite is estimated to be 3.9 m^2/g and 6.1 m^2/g respectively. The surface area estimation has been done under the assumption that the polymer molecules adsorb with a random coil conformation, which is discussed next.

Conformation of the Adsorbed Polymer

The difficulty to study the conformation of adsorbed PEO molecules on dolomite and apatite surface by any of the known techniques such as, NMR, infrared and raman spectroscopy, viscometry, etc., is due to the high porosity of the solids and their appreciable dissolution. Conformation of the adsorbed polymer molecule, at best can be inferred by estimating the area occupied by the polymer molecules on the surface ("parking area"). Indication of the adsorbed layer orientation, may be obtained by determining the effect of molecular weight on adsorption density. The adsorption behavior of polymers from solution onto solids can be summed up by the following expression [Lip74, Sat80, Daw82]

$$\Gamma_m = k\, M^{\bar{a} - 1} \qquad (6.4)$$

where Γ_m corresponds to the saturation adsorption concentration (moles/m^2), M is the molecular weight of the adsorbed polymer and K and $\bar{a}$ are constants, the latter being a function of the conformation of the polymer molecule when it is adsorbed at the interface. According to Perkel and Ullman [Per61] if (i) $\bar{a}$ is 0, the polymer adsorbed is flat on the surface, therefore, the amount of polymer adsorbed ($A = M x \Gamma_m$) is independent of the molecular weight; (ii) $\bar{a}$ is equal to 1, the amount adsorbed is directly proportional to the molecular weight of the polymer indicating a single point attachment of the polymer on the surface; (iii) the polymer molecules are tangled and intertwined at the surface then there is non-uniform segment distribution corresponding to $\bar{a} = 0.5$, and (iv) $\bar{a}$ is between 0 and 0.2, the polymers adsorb as set of contiguous spheres with size proportional to the radius of gyration, representing random-coil conformation. Clearly the smaller the value of $\bar{a}$, the flatter is the conformation of the adsorbed polymer.

A straight line as shown in Figure 6.10, is obtained for log Γ_m versus log M for PEO adsorption an apatite and dolomite particles. The value of $\bar{a}$ is 0.07 for apatite and 0.12 for dolomite indicating a flatter albeit a random coil conformation of the polymer on apatite as compared to dolomite surface. This is surprising for PEO of molecular weight 3400, as it has a rather low degree of coiling (~10)in solution. Dawkins et al. [Daw82] found a significantly higher value of $\bar{a}$ (0.25-0.52) for a similar molecular weight PEO adsorption on silica from water and organic liquids. Scheutjens and Fleer [Sch82], however, argued that such a high dependence of adsorption on molecular weight cannot be explained theoretically. The low dependence of saturation adsorption on molecular weight determined in the present study is in agreement with the theoretical considerations.

To predict the saturation adsorption density for a polymer adsorbing with a random coil conformation, the surface coverage by one molecule needs to be estimated. This can be done using a model proposed by Tronel-Peyroz [Tro83], an improvement on an earlier model by Kirkwood and Riseman [Kir54], which yields the following expression;

$$S^{e} = \frac{(0.67)^{2}\pi}{5.97\phi^{\frac{2}{3}}} M_w^{\frac{2}{3}} [\eta]^{\frac{2}{3}} \tag{6.5}$$

where S^{e} is the surface area occupied by a molecule; ϕ is the Florry-Huggens parameter and $[\eta]$ is the intrinsic viscosity of the polymer. A good agreement is obtained for PEO adsorption on apatite (considering not all of the surface is covered by the polymer) while a significantly lower adsorption is predicted for dolomite (see Table 6.3). The reasons for

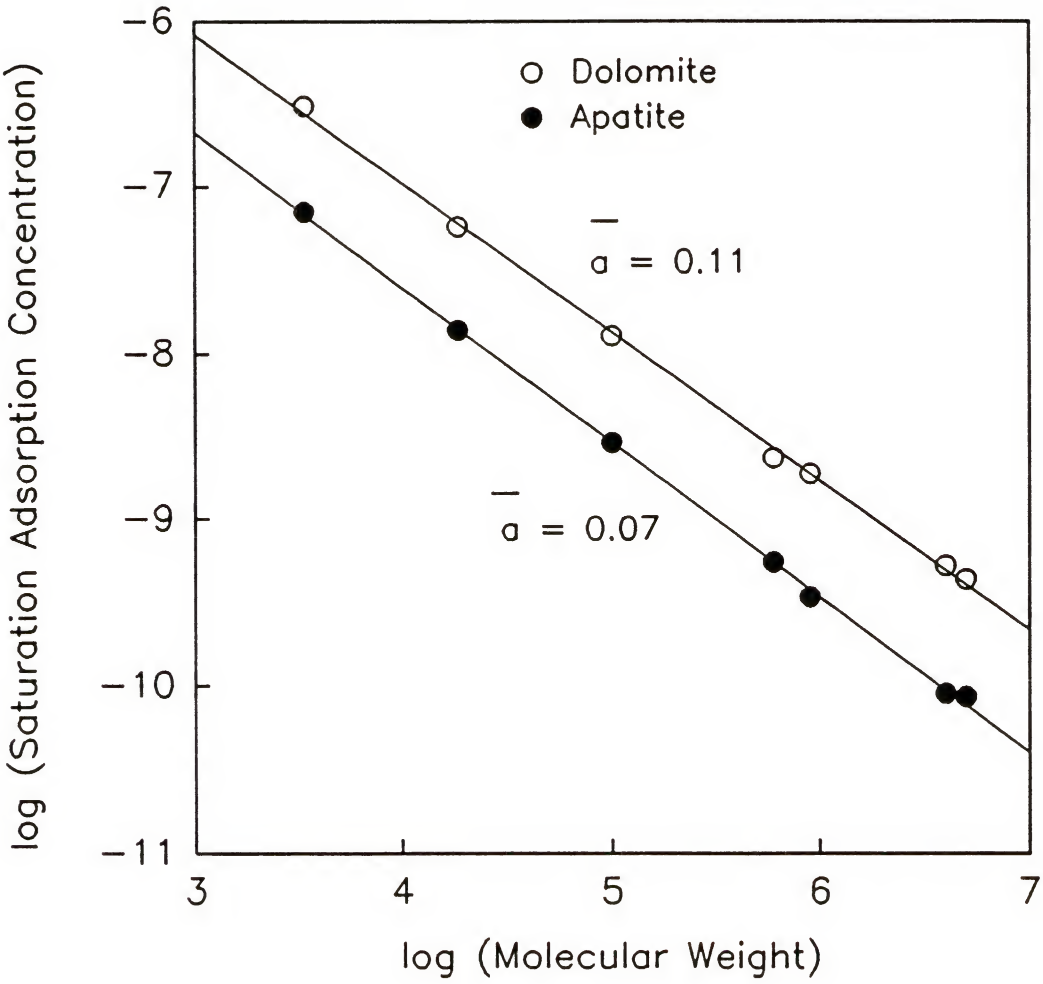


Figure 6.10: Variation Of log Γ_m (Saturation Adsorption Density) With log M (Molecular Weight Of The Polymer).

Table 6.3: Comparison Of The Theoretical And Experimental Saturation Adsorption Densities Of PEO On Dolomite And Apatite.

Molecular Weight	Area Occupied by One Molecule, S^e, nm^2	Saturation Adsorption, mg/m^2		
		Theoretical	Apatite*	Dolomite*
5.00 X 10^6	28903	0.29	0.43	2.18
1.00 X 10^5	22408	0.30	0.36	2.10
9.00 X 10^5	3781	0.31	0.33	1.69
9.00 X 10^5	2338	0.43	0.31	1.41
1.00 X 10^5	281	0.61	0.25	1.28
1.85 X 10^4	37.9	0.81	0.25	1.07
3.40 X 10^3	6.84	0.82	0.24	1.04

* Experimental

the observed discrepancy in PEO adsorption on dolomite are discussed below.

Fleer et al. [Fle83] and Blaakmeer [Bla90] have suggested that the saturation adsorption is about 2 to 5 times the equivalent monolayer, primarily due to compaction of the polymer molecule at high adsorption densities. It should be noted that, the equilibrium adsorption measurements are made at higher concentrations, therefore, elongated conformation of the polymer on the solid surface may be expected [Nap83, Eir83]. This would indirectly lead to a higher polymer adsorption density, as compared to the theoretically predicted value based on the radius of gyration. Further, adsorption of high molecular weight PEO on dolomite in this study is measured for flocculating particles. Therefore, the polymer may be considered to be further elongated, since it is stretched with anchoring points on different particles. This would imply that adsorbed polymer molecule would occupy at least two sites (on flocculating particles) as compared to one otherwise. Considering the uncertainties of the adsorption models developed thus far to explain surface coverage and adsorbed conformation in literature [Fle83], and complications due to simultaneous flocculation, a higher adsorption density, as observed may be possible.

Correlation With The Mathematical Model

Adsorption

The equilibrium adsorption density as a function of the molecular weight of the polymer is plotted in Figure 6.11. The observed trends of a straight line variation of saturation adsorption on dolomite with log of molecular weight, is in agreement with earlier data by Fleer et al. [Fle83] and Van der Linden et al. [Van78a, Van78b]. Fleer et al. [Fle83] have shown both experimentally and computationally, that the amount of the

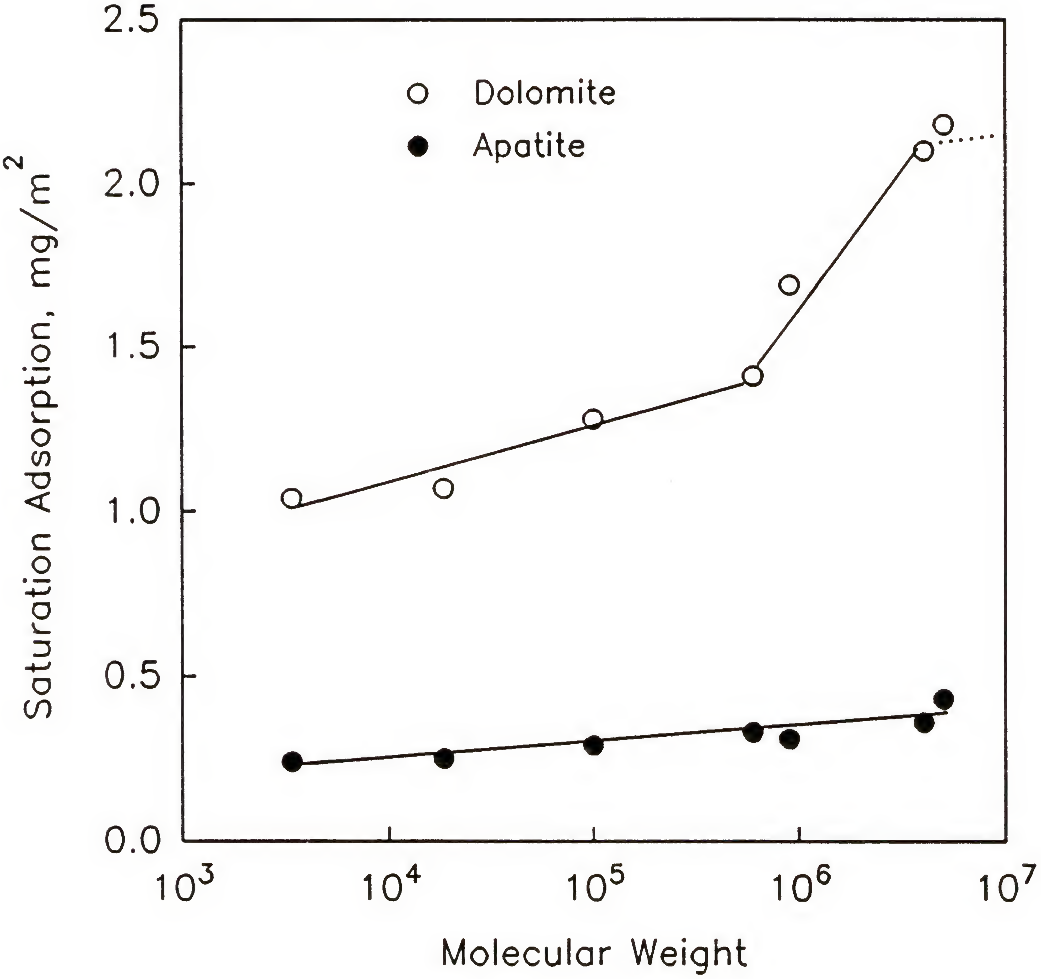


Figure 6.11: Equilibrium Adsorption Density As A Function Of Molecular Weight.

polymer adsorbed increases slightly with the log of the molecular weight. A much sharper increase, however, was reported by Van der Linden et al. [Van78a, Van78b], for a wider range of polymer molecular weights. In the present study, adsorption on apatite follows the trends indicated by Fleer et al. [Fle83]. However, for dolomite adsorption is in agreement with the model proposed by Fleer et al. [Fle83] for only low molecular weight polymers, followed by a steep increase, as observed by Van der Linden [Van78a, Van78b] for another system. Higher uptake of the larger molecular weight polymer may be expected primarily because of a stronger driving force for adsorption. According to equation (6.4), on increasing the molecular weight of the polymer, the amount adsorbed (weight) would approach a constant value. Physically, this plateau region would imply, total coverage of the surface by the polymer. In the case of PEO adsorption on dolomite, the plateau region is attained at about 5 million molecular weight (See Figure 6.12). Under these conditions, it may be assumed that the entire surface is active or the ratio of the active sites to the total number of sites is one, i.e., $\Phi = 1$. This verifies the assumption by Moudgil et al. [Mou87c, Mou89b, Mou91] that Φ is 1 for PEO adsorption on dolomite. It should be noted that for apatite, the plateau region is observed at a much lower molecular weight, implying a much flatter conformation of the adsorbed polymer.

It has been explained earlier that the number of active sites for polymers of different molecular weight are related according to the area occupied by the molecule and the saturation adsorption density. Therefore, the adsorption data for a given surface can be used to derive the values of Φ for different molecular weight polymers. This can

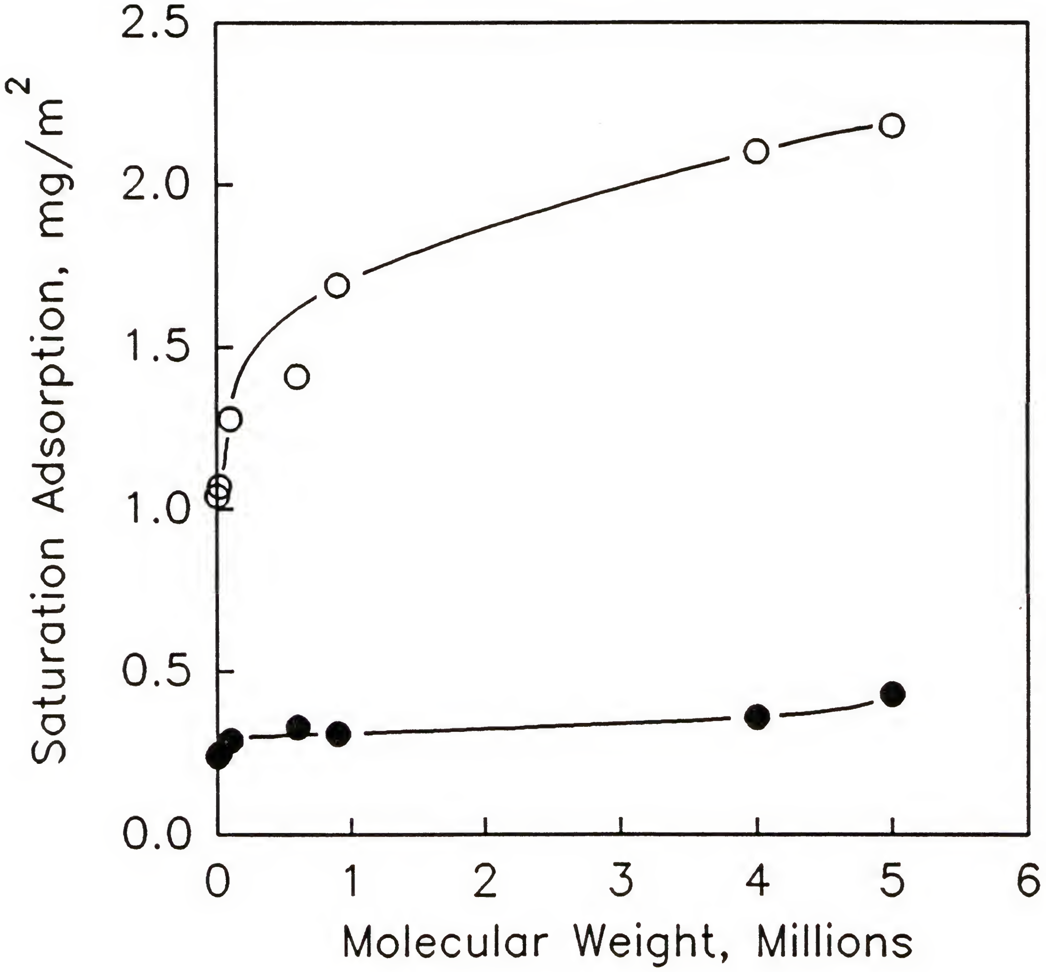


Figure 6.12: Equilibrium Adsorption Density Showing A Plateau Region As A Function Of Molecular Weight.

be estimated by using the expression (5.15) defined in Chapter 5. Substituting γ for PEO as 0.78 [Bai76], this expression would reduce to

$$\frac{\bar{\Phi}}{\Phi} = \frac{x}{X}\left[\frac{m}{M}\right]^{0.18} \qquad (6.6)$$

where x,X = Adsorption density (g/m^2) of the polymer of molecular weights m and M respectively. Clearly, $\bar{\Phi}$ would be smaller than Φ. The physical significance of $\bar{\Phi}$ is that lower molecular weight polymers have smaller area available for adsorption.

It has been shown that the saturation adsorption on apatite is smaller than on dolomite. This can be explained by two different reasons, the first being that the conformation of the polymer molecule on apatite surface is stretched, or the surface of apatite has less number of active sites as compared to dolomite. The conformation on both apatite and dolomite was earlier inferred to be random coil, however, the value of $\bar{a}$ suggests that polymer adsorbs with a flatter conformation on apatite surface. It can be further argued from equation (6.4) that the amount of polymer adsorbed scales as $M^{0.07}$ for apatite and as $M^{0.12}$ for dolomite, implying that the total coverage of the apatite surface (saturation adsorption) may be obtained at a much lower molecular weight as compared to dolomite (see Figure 6.12). In other words $\bar{\Phi}$ is 1 for PEO adsorption on apatite. This would lead to the argument that Φ, by definition should also be 1.0 for apatite surface, which clearly would not explain the absence of flocculation of apatite particles. This implies that the estimation of the active and total sites on the apatite surface, which was based on the saturation adsorption on dolomite particles (under the assumption of similar conformation) [Mou87c, Mou89b, Mou91], may not be accurate. In order to incorporate the difference in the polymer conformation on the different surfaces, the definition of a site and active site on the inert component needs to be redefined in terms of the sites on the active component. Since the active component flocculates, the reference site is equivalent to the size of the adsorbed polymer molecule under saturation conditions. This reference site, combines both aspects of size and the conformation of the adsorbed polymer. The adsorption density of the polymer on the inert component is then reduced to the "equivalent" sites, by the same mathematical relation as defined earlier by Moudgil et al. [Mou89b, Mou91].

Considering the definition of the equivalent sites, the numerical values obtained for Φ earlier by Moudgil et al. and in this paper do not change. The saturation adsorption and Φ for different molecular weight polymers on apatite and dolomite given in Table 6.4 show that the effective Φ for apatite surface, as expected, is much lower as compared to that of dolomite particles.

Surface coverage (θ) by the various polymers on dolomite and apatite at different dosages can be obtained from the non-equilibrium and the equilibrium adsorption isotherms discussed earlier in this chapter. It should be realized that θ refers to the fraction of the active sites covered and not the actual surface coverage. Surface coverage of dolomite and apatite by PEO molecular weights 5 million, 600,000 , 100,000, 18,500 and 3,400 respectively is plotted in Figures 6.13-6.17. A steeper rise in the surface coverage on apatite as compared to dolomite with increase in polymer dosage for lower molecular weight PEO (SBA) is observed (See Figure 6.14-6.17), implying that the blocking of sites on the apatite particles would be similar by the different SBA molecules. It should, however, be noted that a meaningful surface coverage by the SBA would be in terms of the blocked surface for flocculant adsorption. This can be estimated by the site blocking parameter, defined as a product of $\bar{\Phi}$ and $\bar{\theta}$. Physically, the site

Table 6.4: Equilibrium Adsorption Of PEO On Apatite And Dolomite.

Polymer Molecular Weight	Dolomite		Apatite	
	Γ_m, mg/m^2	Φ	Γ_m, mg/m^2	Φ
5.00 X 10^6	2.18	1.00	0.43	0.20
1.00 X 10^5	2.10	0.92	0.36	0.18
9.00 X 10^5	1.69	0.56	0.31	0.10
9.00 X 10^5	1.41	0.44	0.33	0.10
1.00 X 10^5	1.28	0.29	0.29	0.04
1.85 X 10^4	1.07	0.18	0.25	0.04
3.40 X 10^3	1.04	0.13	0.24	0.03

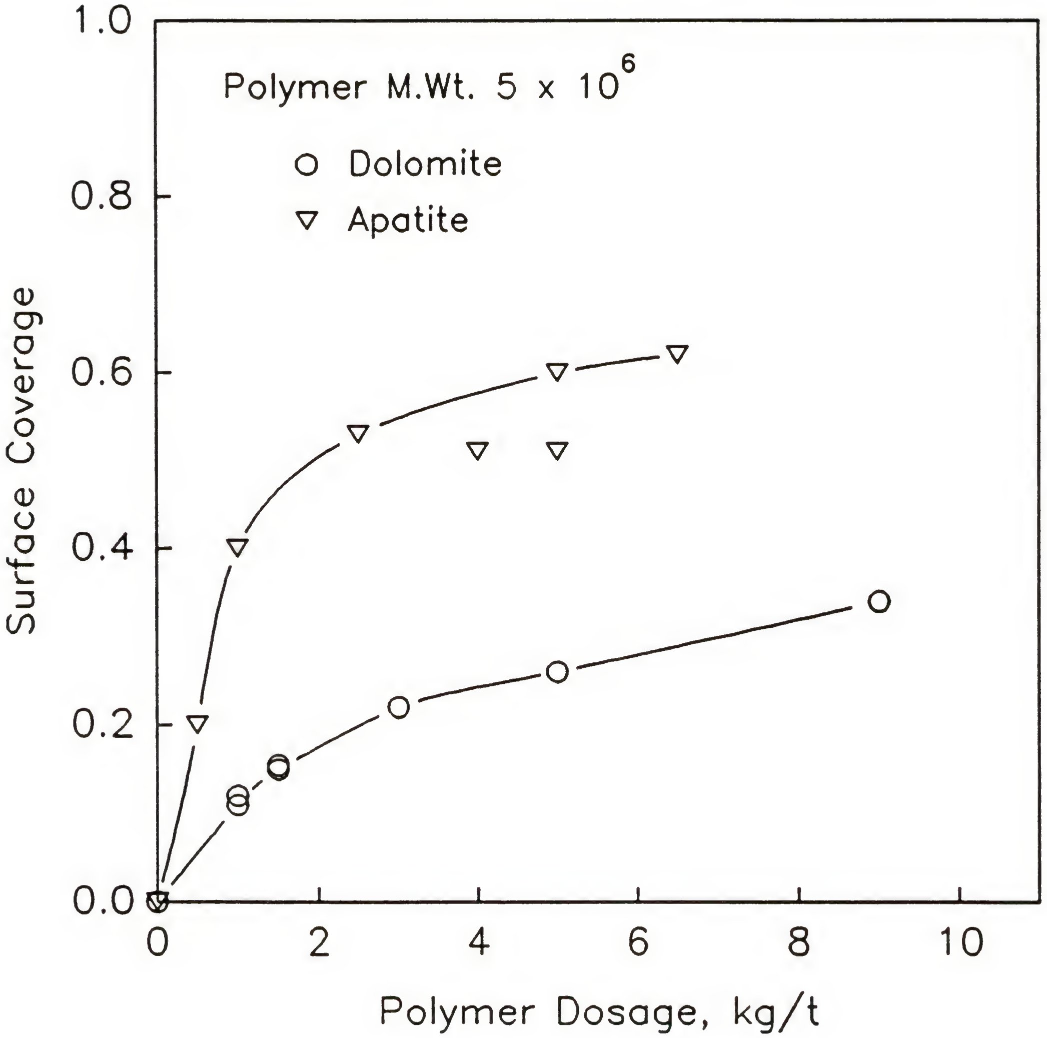


Figure 6.13: Effective Surface Coverage Of Apatite And Dolomite Surface By PEO Of Molecular Weight 5 X 10^6.

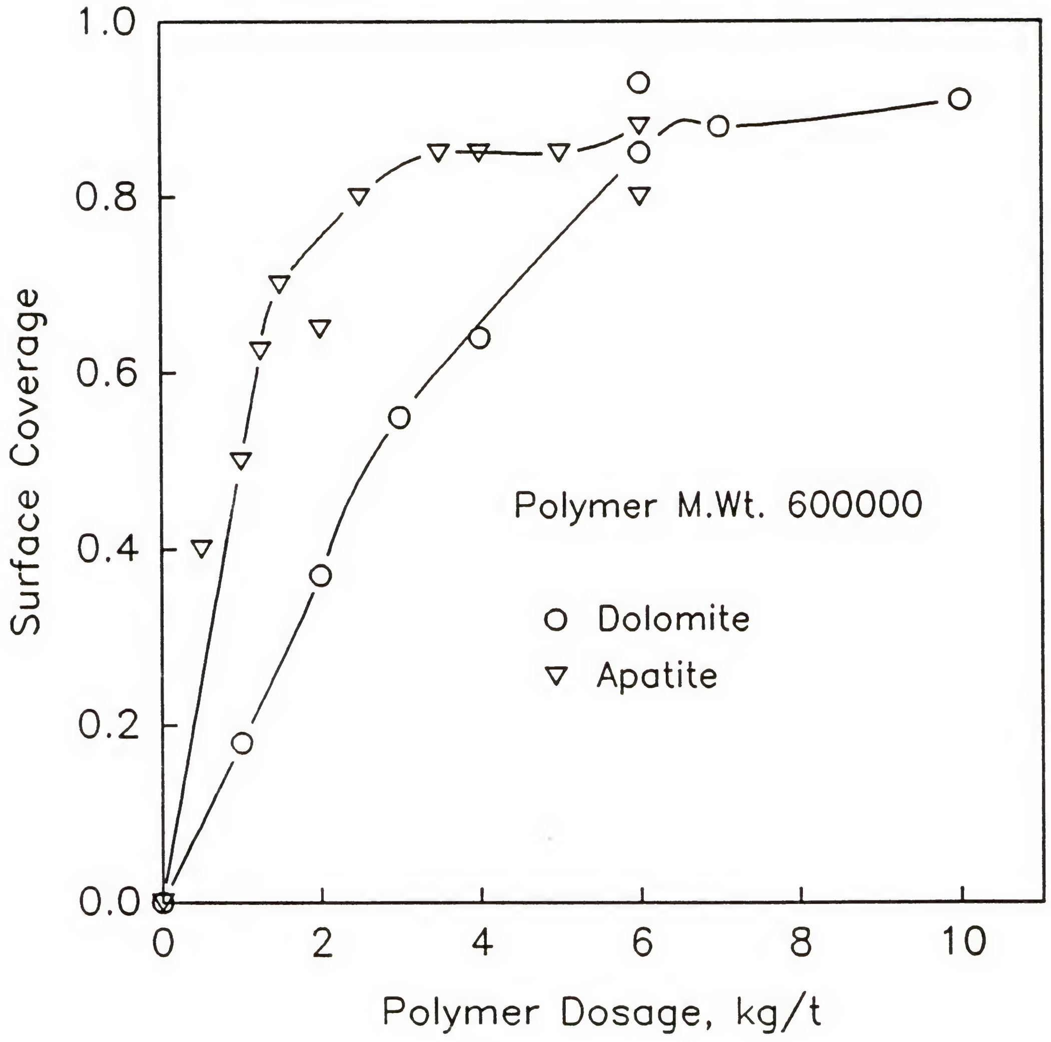


Figure 6.14: Effective Surface Coverage Of Apatite And Dolomite Surface By PEO Of Molecular Weight 6 X 10^5.

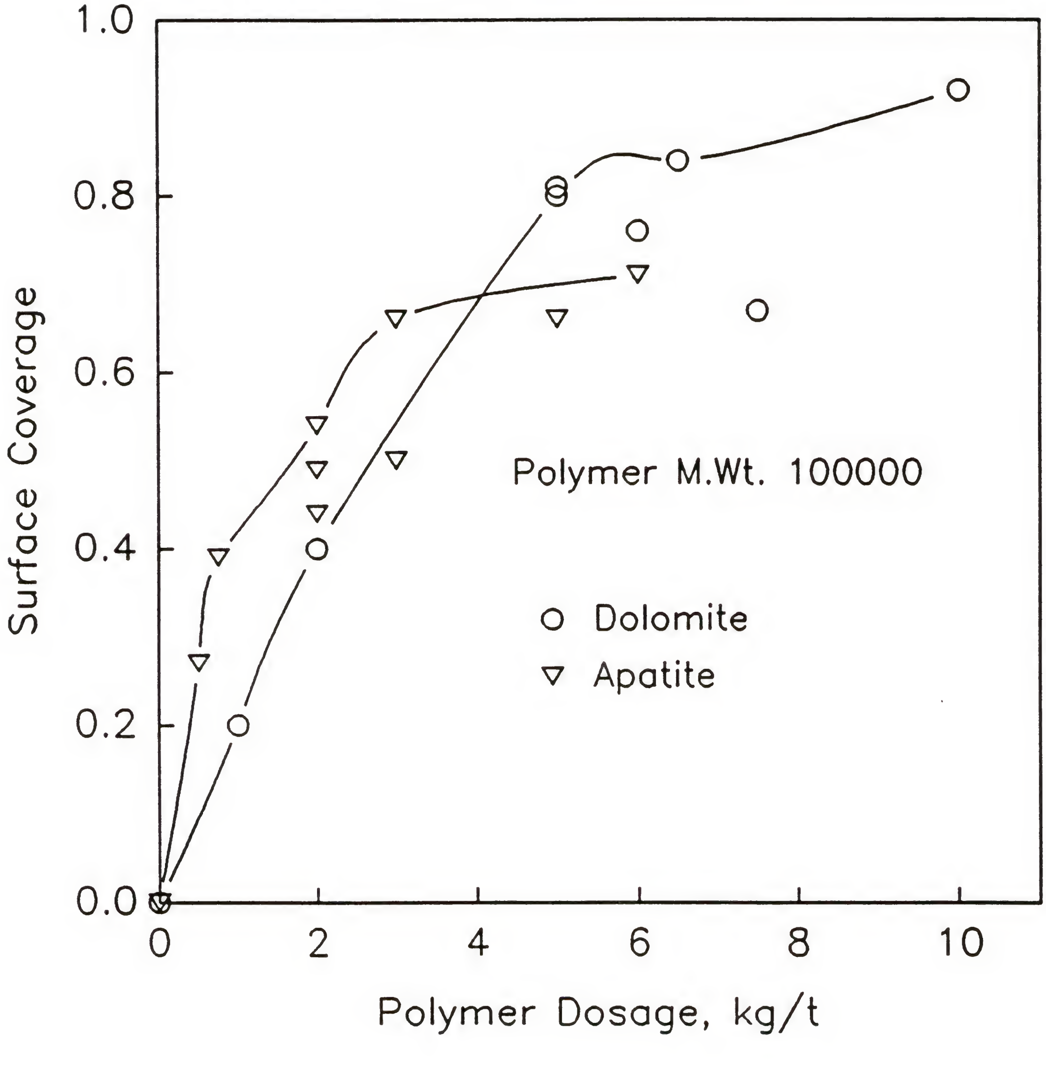


Figure 6.15: Effective Surface Coverage Of Apatite And Dolomite Surface By PEO Of Molecular Weight 1 X 10^5.

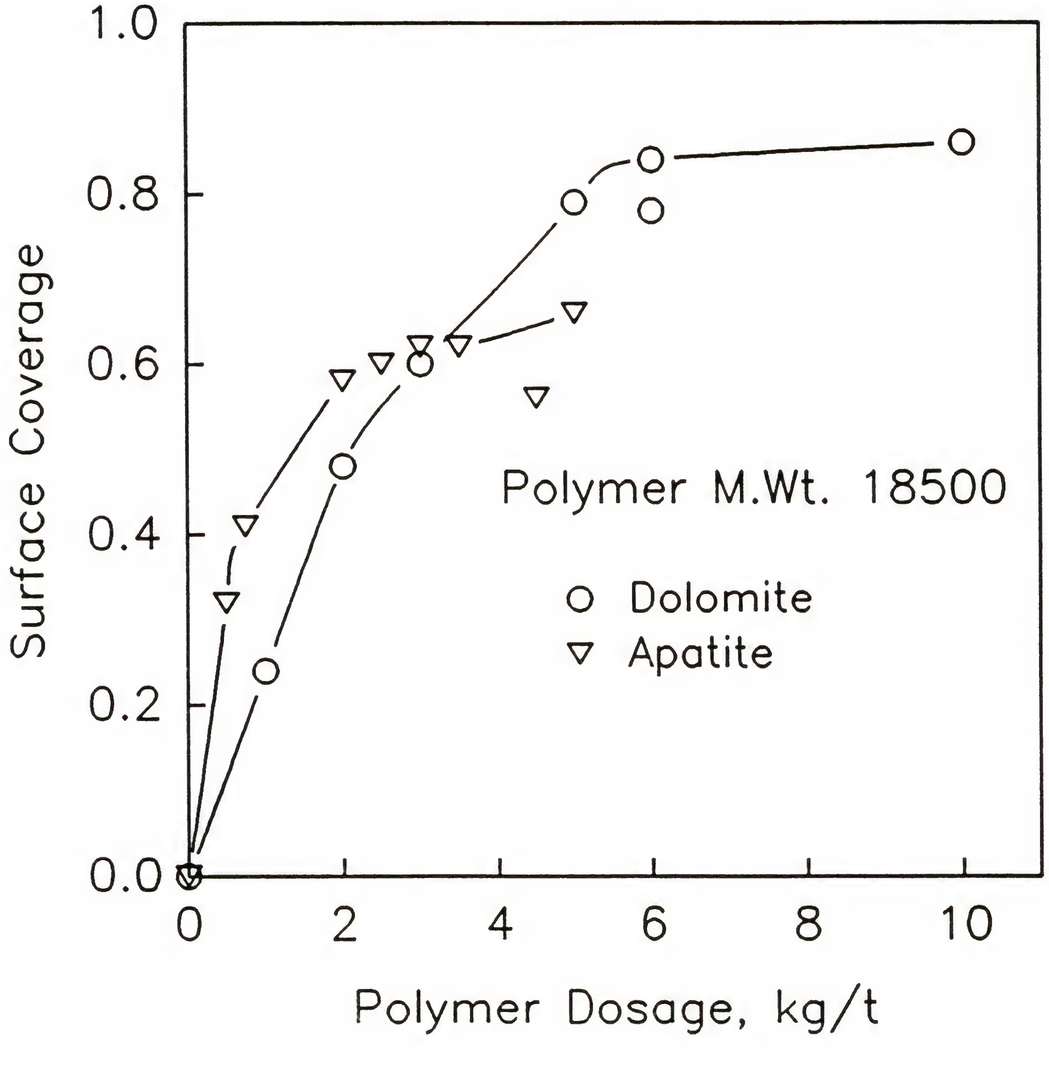


Figure 6.16: Effective Surface Coverage Of Apatite And Dolomite Surface By PEO Of Molecular Weight 1.85 X 10^4.

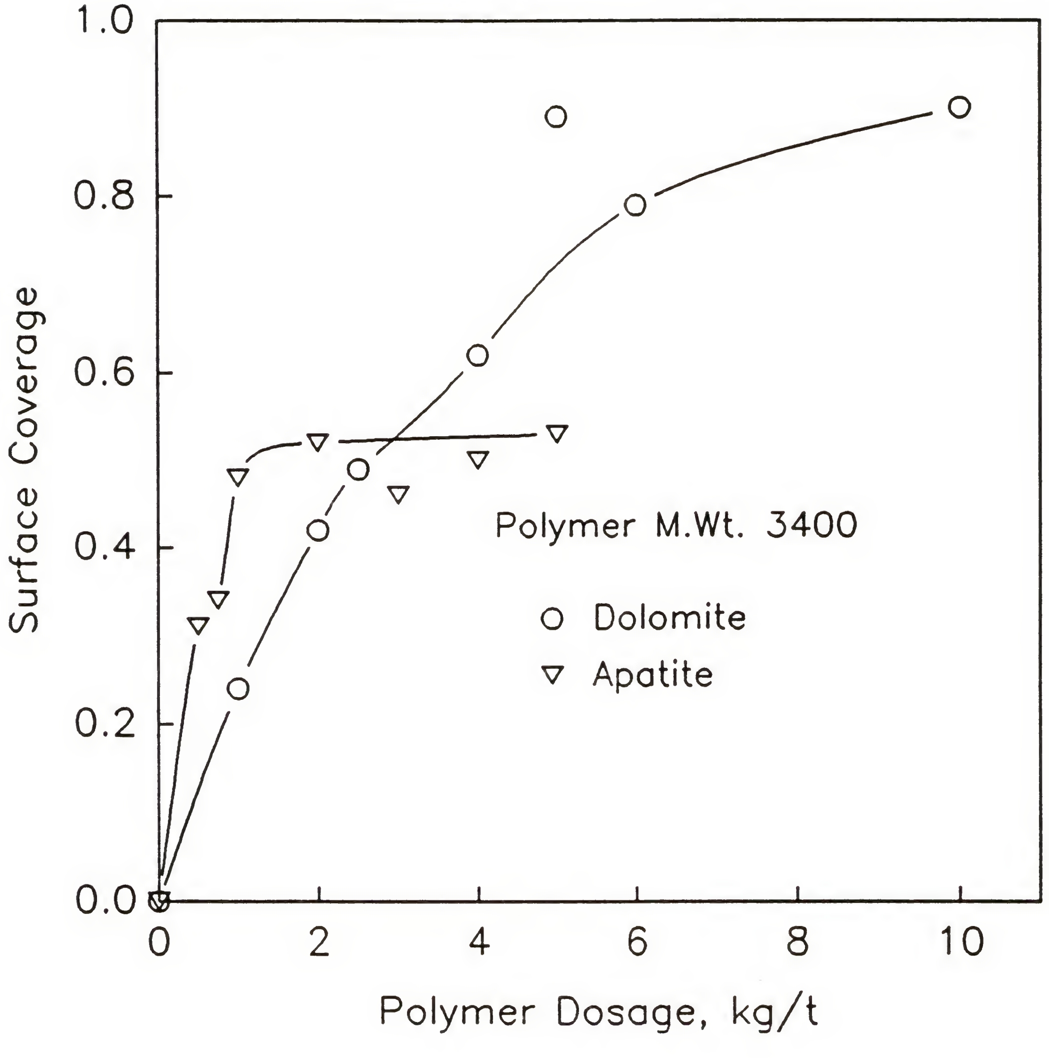


Figure 6.17: Effective Surface Coverage Of Apatite And Dolomite Surface By PEO Of Molecular Weight 3.40 X 10^3.

blocking parameter is the total surface which the SBA is capable of blocking for the flocculant adsorption. It can be inferred from the above arguments and Figures 6.14-6.17 that the site blocking parameter is a stronger function of $\bar{\Phi}$, or the molecular weight of the SBA. Similar observations can be made for dolomite, at low SBA dosages. However, at higher SBA dosages, more surface on dolomite seems to be covered as compared to apatite. This may be attributed to the difference in the kinetics of adsorption from a concentrated polymer solution.

Effect of site blocking agent on single mineral flocculation

The effect of SBA dosage and molecular weight on flocculation of dolomite can be explained by the model described earlier (See Chapter 5). The amount of dolomite flocculated as a function of $\bar{\theta}$ (surface coverage of SBA) is given in Figure 6.18. It can be seen that as the value of $\bar{\theta}$ increases for a constant molecular weight polymer ($\bar{\Phi}$), the flocculation decreases linearly. This can be attributed to the fact that the collision efficiency factor also decreases linearly with $\bar{\theta}$. Further, the amount of flocculation plotted as a function of the site blocking parameter (product of $\bar{\theta}$ and $\bar{\Phi}$) also varies linearly. In fact, the data of Figure 6.18 compresses to one straight line as plotted in Figure 6.19. This has a major practical significance, as it shows a direct relation between the dosage and the molecular weight of the SBA on depression of flocculation. The flocculation of dolomite is extensive and it can be inferred from the slope of the line in Figure 6.19 that it is not possible to theoretically block all the active surface sites on dolomite by a SBA. Therefore, irrespective of the SBA molecular weight and dosage, the flocculation on dolomite cannot be suppressed. Further, it is to be noted that half the dolomite surface coverage by the flocculant cannot be obtained within two minute conditioning time. Therefore, maximum flocculation for dolomite cannot be experimentally realized. This

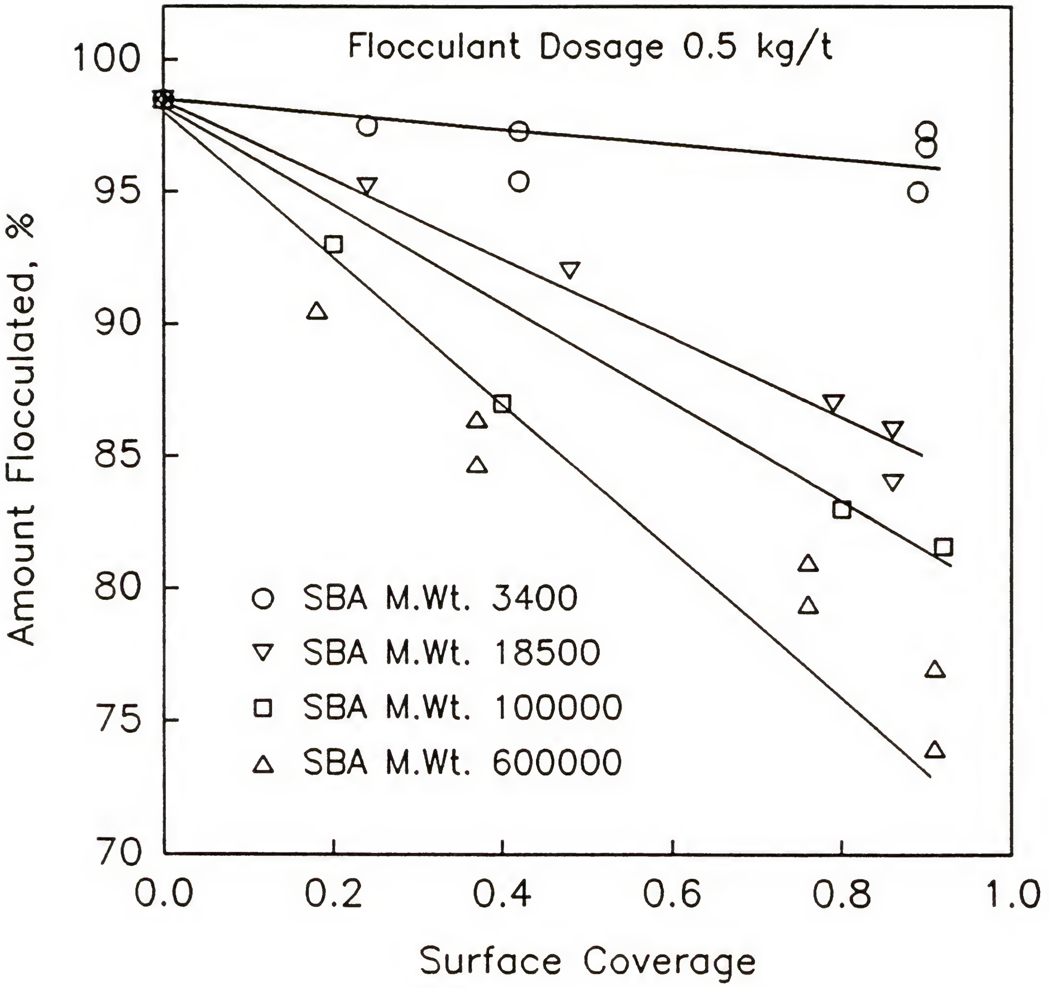


Figure 6.18: Flocculation Of Dolomite As A Function Of Surface Coverage By The Site Blocking Agent.

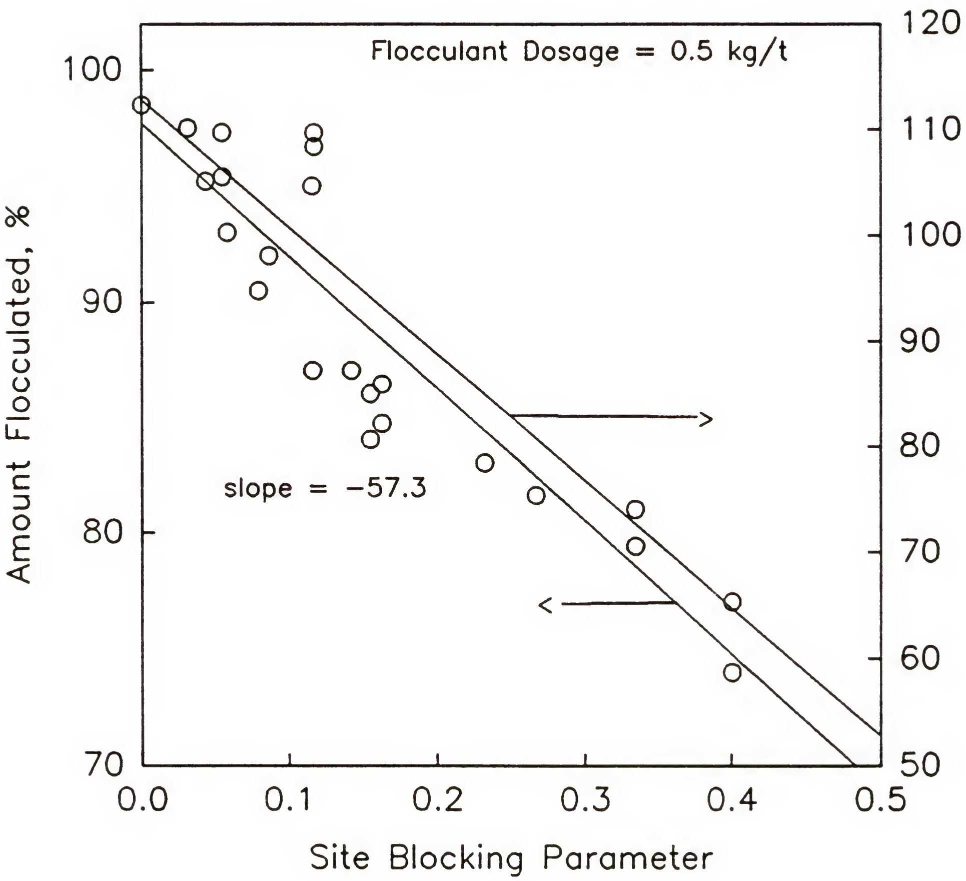


Figure 6.19: Correlation Between Dolomite Flocculation And Site Blocking Parameter ($\Phi\theta$).

may be true in general, considering the high dosage requirements to achieve half surface coverage of dolomite.

In case of apatite although no flocculation is observed but in the presence of the SBA the collision efficiency factor is reduced quite significantly. However, E_{ii} is below the critical collision efficiency factor, therefore, no flocculation can be observed with or without the SBA. This is observed experimentally.

Effect of site blocking agents on mixed mineral flocculation

Selectivity in floc formation can also be represented in terms of selectivity ratio, which is defined as the ratio of apatite to dolomite in the flocs. The higher the ratio, the greater the extent of heteroflocculation and vice versa. This representation is necessary because the collision efficiency is described in terms of floc formation of pure dolomite and that of apatite-dolomite mixture. The selectivity (in terms of ratio of apatite/dolomite in flocs) is plotted as a function of the ratio of collision efficiency factors for heteroflocculation and flocculation of only dolomite (E_{ij}/E_{ii}), in Figure 6.20. Increase in the site blocking parameter ($\bar{\Phi}\bar{\theta}$), decreases the E_{ij}, hence less heteroflocculation is observed. The above treatment helps in normalizing the data with respect to different dosages of the flocculant and the SBA.

Concept of "Equivalent Active Sites"

Flocculation is often directly correlated with the polymer adsorption on solid particles. It is believed that if a polymer significantly adsorbs on a material, then its higher molecular weight fraction can be used as a flocculant. For example, it has been shown earlier that a 5 million molecular weight polyethylene oxide (PEO) flocculates dolomite, while it is dispersed with PEO 100,000 molecular weight. However, the same

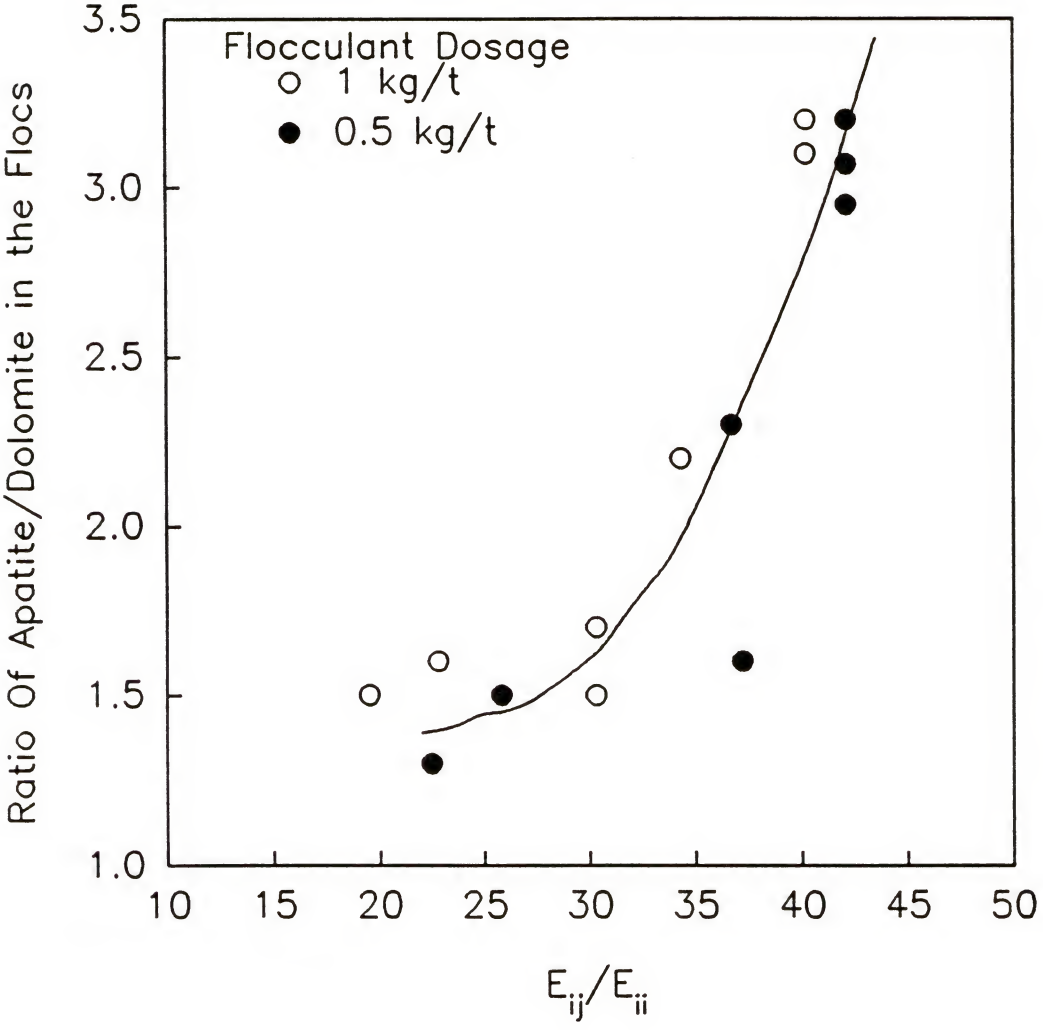


Figure 6.20: Ratio Of % Apatite/% Dolomite In The Floc Bed As A Function Of E_{ii}/E_{ij}.

flocculant may not be capable of flocculating another material (e.g., apatite) even if it adsorbs on it indicating that the correlation between adsorption and flocculation may not be as straight forward as it is generally assumed to be. For example, apatite, quartz and alumina do not form flocs even with 5 million molecular weight PEO [Mou87c]. This implies that there exists a critical molecular weight for flocculation with a polymer, which is a function of the surface property of the mineral. It is widely acknowledged that the saturation adsorption of the polymer is significantly lower on the solids that are dispersed as compared to the particles that can be flocculated [Mou87c]. Smaller adsorption on the non-flocculating material as compared to the flocculating material was believed to be responsible for dispersion in such cases. It was further postulated that fewer active sites exist on the non-flocculating component [Mou87c]. The small adsorption density on the non-flocculating component may be attributed to (i) fewer sites or (ii) a flatter conformation of the adsorbed polymer. Tjipangandjara and Somasundaran [Tji91], Somasundaran and Ramachandaran [Som88], Rubio and Kitchener [Rub76], Fleer et al. [Fle83], Clark and Lal [Cla82] and Lal and Stepto [Lal77] have shown that flocculation is inhibited when conformation of the adsorbed polymer is relatively flat. Further, Tjipangandjara and Somasundaran [Tji91], Lal and Stepto [Lal77] and Tronel-Peyroz et al. [Tro83] have shown that low molecular weight polymers (1000-20000) tend to acquire a flatter conformation on the solid surfaces as compared to high molecular weight polymers. The low molecular weight fractions of a flocculant, therefore, may not be capable of flocculation.

In the model developed by Moudgil et al. [Mou87c, Mou89b, Mou91] (described in Chapter 2) to study flocculation, the ability for floc formation is examined using a collision efficiency factor (E_{ij}) which is defined by expression (5.1)

$$E_{ij} = \Phi_i \Phi_j \, [\theta_i(1 - \theta_j) + \theta_j(1 - \theta_i)]$$

This expression is based on the number of active sites, assuming that the polymer conformation on the different surfaces is same [Mou87c, Mou91]. It has been shown earlier that there exists a critical collision factor above which flocculation is observed [Mou91]. As explained earlier in this chapter, this theory was further improved to incorporate the differences in the conformation of the adsorbed polymer. Φ for a material is estimated from the saturation adsorption data with respect to a reference material, the entire surface of which is considered as active. On the other hand, θ is the ratio of the non-equilibrium and saturation adsorption values for a particular mineral.

In order to account for smaller saturation adsorption on the non-flocculating particles, it is necessary to introduce the concept of "equivalent active sites". The concept of equivalent active sites is important in determining the active sites for the lower molecular weight fraction of the flocculant. This involves reducing the adsorption density on the inert component to the number of polymer molecules adsorbed (measure of the number of sites) on the surface, with the same size and conformation as that on the active material. In other words it is a site equivalent to the site for the same polymer molecule on a reference surface. The reference material, as mentioned above, is the material which exhibits good flocculation. In other words, if strong flocculation is observed in one material then the conformation of the polymer and the fraction of the sites considered active on that surface are taken as a standard. Clearly if the adsorption is smaller due to flatter conformation, less binding sites or any other reasons, the equivalent active site fraction would also be smaller. This would account for both the conformation and the number of sites for the polymer adsorption at the same time without any ambiguity. Saturation adsorption, therefore, is a measure of the combination of these two parameters namely amount and the conformation of the adsorbed polymer. The choice of the reference material is not completely arbitrary and has been discussed earlier. Definition of Φ in this manner does not affect the conclusions of the earlier defined model. Flocculation of apatite and six dolomite samples with PEO of different molecular weights was studied. The dolomite samples, as shown in Figure 6.21, exhibited different flocculation behavior. No flocculation was observed for dolomite samples A, B, C, D with a lower molecular weight PEO but significant flocculation occurred with PEO beyond a certain molecular weight of the polymer. Dolomite samples E and F exhibited no tendency towards floc formation irrespective of the molecular weight of the PEO. Also, the apatite sample did not flocculate in the range of molecular weights examined.

Adsorption and flocculation results at a dosage of 1 kg/t of the polymer indicate a direct correlation between flocculation and saturation adsorption (See Table 6.5). Dolomite sample A flocculated very strongly and the value of Φ, as explained earlier, is chosen as 1 for this material. The saturation adsorption values (Γ_m) of various molecular weights of PEO/PEG on the mineral surfaces are listed in Table 6.6.

The estimation of the ratio of active sites, on the surface as explained earlier, was done on the basis of dolomite sample A surface being completely active (Φ = 1 for 5 million molecular weight PEO). The method of estimation of Φ remains the same as was suggested earlier by Moudgil et al. [Mou87c]. The Φ for the lower molecular weight polymers is estimated using the expression 5.15. This expression is based on the assumption that number of sites are related to the ratio of respective parking areas and hence it is a measure of radius of gyration and the molecular weight of the polymers.

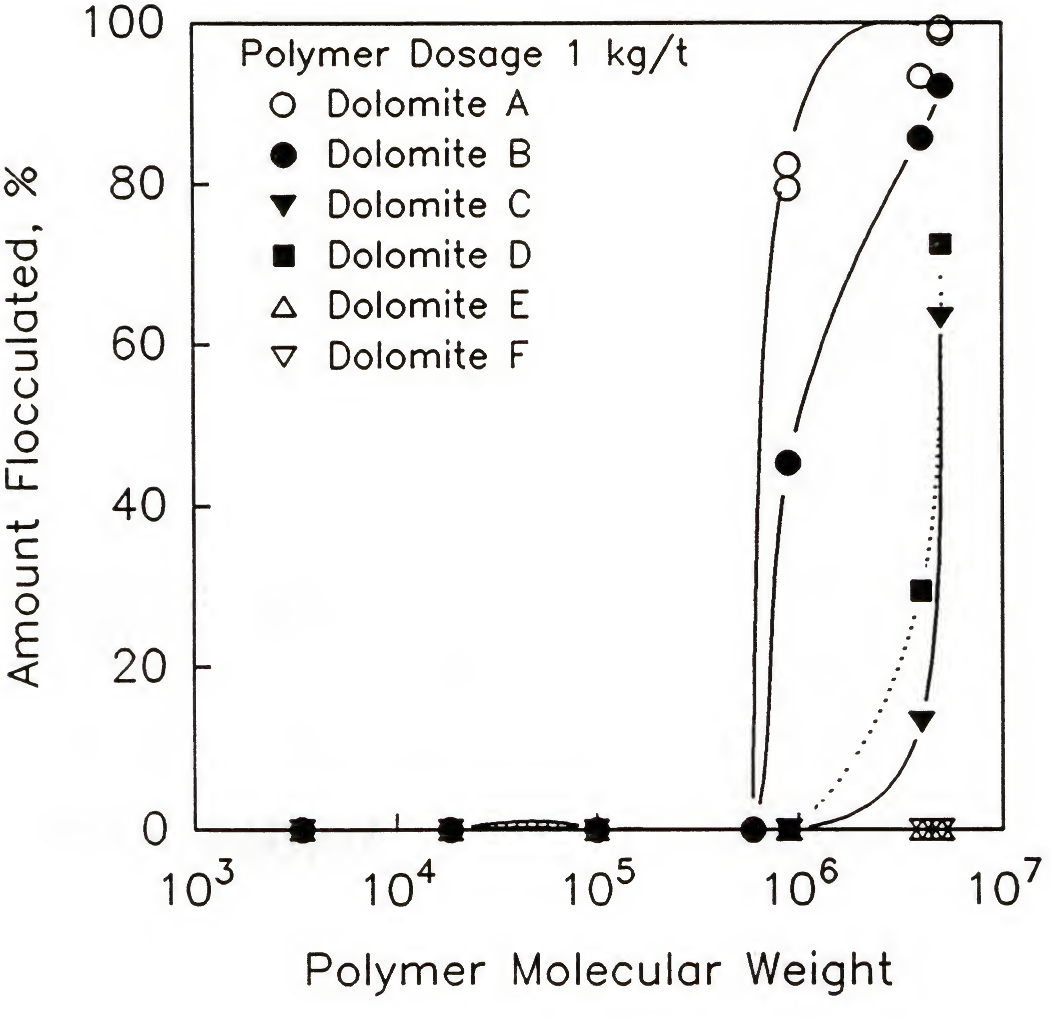


Figure 6.21: Flocculation Behavior of Different Dolomite Samples With PEO.

Table 6.5: Correlation Between Saturation Adsorption Density And Flocculation.

Flocculant Molecular Weight = 5 Million

Polymer Dosage = 1.0 kg/t

Mineral	Saturation Adsorption Density, mg/m^2	Amount Flocculated, %
Dolomite A	2.18	98.5
Dolomite B	1.93	92.5
Dolomite C	1.16	69.3
Dolomite D	1.19	72.5
Dolomite E	0.39	0
Dolomite F	0.39	0
Apatite	0.40	0

Table 6.6: Equilibrium Adsorption Of PEO On Various Dolomite Samples.

Molecular Weight	Dolomite "B"		Dolomite "C"		Dolomite "D"		Dolomite "E"		Dolomite "F"	
	Γ_m, mg/m^2	Φ	Γ_m, mg/m^2	Φ	Γ_m, mg/m^2	Φ	Γ_m, mg/m^2	Φ	Γ_m, mg/m^2	Φ
5.00 X 10^6	1.93	0.88	1.16	0.53	1.19	0.55	0.58	0.39	0.35	0.16
4.00 X 10^6	1.54	0.68	1.05	0.14	1.05	0.46	0.70	0.31	-	-
9.00 X 10^6	1.37	0.47	0.58	0.09	0.90	0.31	0.72	0.24	-	-
6.00 X 10^5	1.37	0.33	0.60	0.20	0.68	0.22	0.60	0.19	0.20	0.07
1.00 X 10^5	1.00	0.23	-	-	-	-	0.62	0.14	-	-
1.85 X 10^4	0.73	0.12	-	-	-	-	0.58	0.09	-	-
3.40 X 10^3	0.65	0.08	-	-	-	-	0.55	0.07	-	-

The values of estimated Φ are also listed in Table 6.6.

It appears that flocculation is observed only when the value of Φ is about 0.40 (which corresponds to a maximum value of E_{ij} to be 0.1). For example, no flocculation is observed for dolomite Sample E, F and apatite even with a 5 million molecular weight flocculant. It is, however, easier to correlate flocculation with this critical value of Φ than with the collision efficiency factor, defined earlier, because of the linear dependance of E_{ij} on lower value of surface coverage (Θ). The most important consequence of this approach is in understanding the selective flocculation process, for example, the value of Φ in a mixture could indicate whether separation by selective flocculation is possible or not. If Φ for mixed flocculation is greater than the critical value then the mixture would co-flocculate, otherwise only flocs of single components would be formed. Effective Φ for a mixture can be calculated by the following expression

$$\phi_{effective} = \sqrt{\phi_i \phi_j} \tag{34}$$

where

Φ_i, Φ_j = Φ of material *i* and *j* respectively

In the present study the effective Φ of dolomite A-apatite and dolomite A-dolomite E are estimated to be 0.45 and 0.62 respectively, which are larger than critical Φ (approximately 0.4). In both these cases complete co-flocculation is observed. This implies that during floc formation the entire mixture acts as a composite surface. To further validate the concept, flocculation of a number of mineral combinations was studied. The minimum molecular weight of the polymer required for co-flocculation and the respective values of $\Phi_{effective}$ are listed in Table 6.7. Accordingly, co-flocculation of

Table 6.7: Molecular Weights For The Advent Of Flocculation In Mixtures Of Various Samples.

Mineral 1 -----> Mineral 2	Dolomite Sample A	Dolomite Sample B	Dolomite Sample C	Dolomite Sample D	Dolomite Sample E	Dolomite Sample F	Apatite
Dolomite Sample A $(\Phi_{effective})$	9 X 10^5 (0.56)	9 X 10^5 (0.51)	4 X 10^6 (0.64)	4 X 10^6 (0.74)	4 X 10^6 (0.53)	$\geq$5 X 10^6 (0.4)	$\geq$4 X 10^6 (0.38)
Dolomite Sample B $(\Phi_{effective})$		9 X 10^5 (0.47)	4 X 10^6 (0.55)	4 X 10^6 (0.56)	4 X 10^6 (0.46)	-	4 X 10^6 (0.44)
Dolomite Sample C $(\Phi_{effective})$			$\geq$4 X 10^6 (0.44)	4 X 10^6 (0.44)	5 X 10^6 (0.46)	>5 X 10^6 (0.30)	>5 X 10^6 (0.32)
Dolomite Sample D $(\Phi_{effective})$				4 X 10^6 (0.46)	5 X 10^6 (0.46)	>5 X 10^6 (0.31)	>5 X 10^6 (0.33)
Dolomite Sample E $(\Phi_{effective})$					>5 X 10^6 (0.39)	>5 X 10^6 (0.25)	>5 X 10^6 (0.27)
Dolomite Sample F $(\Phi_{effective})$						>5 X 10^6 (0.16)	>5 X 10^6 (0.18)
Apatite $(\Phi_{effective})$							>5 X 10^6 (0.20)

dolomite A -dolomite C and apatite-dolomite A is first observed with 4 million molecular weight PEO. It can be inferred from Table 6.7 that dolomite A and apatite can be separated using a 900,000 molecular weight flocculant, since flocculation of only dolomite sample A is observed with this polymer. Selective flocculation was attempted for a 80:20 mixture of apatite and dolomite A and the results presented in Table 6.8 indicate a partial selectivity in this system at a dosage of 1 and 2 kg/t. The low recovery with PEO of 5 million molecular weight indicate co-flocculation of apatite with dolomite, which reports in the +400 mesh fraction. Under these conditions a small amount of apatite remaining in the supernatant can be of high purity since most of the dolomite flocculates, as observed experimentally.

To physically explain the concept of $\Phi_{critical}$, it is to be noted that Φ is a measure of the saturation adsorption density of the polymer on the surface normalized with respect to the conformation and the size of the active site on the reference material. A material with a high Φ implies high affinity for polymer adsorption and formation of strong bridges during the collision process. On the other hand, surfaces with low Φ would signify smaller affinity of the surface for the polymer thereby making bridging difficult. This implies that there is a critical affinity of the polymer for the solid surface for bridging to take place. It was shown by Clark and Lal [Cla82] that in the region of weak adsorption the probability of bridging increases with the polymer-surface interaction energy, whereas in the case of strong adsorption there is a reversal of trends. Therefore, for flocculation to take place it is necessary that the interaction energy of the polymer segment with surface is high and the conformation of the adsorbed polymer is open (polymer adsorption in terms of trains and loops) for better bridging. In other words, both the number of active sites and the conformation are important for flocculation of particles to occur.

Table 6.8: Mixed Mineral Flocculation Of Apatite And Dolomite With PEO Of Molecular Weight 900,000.

Apatite: Dolomite = 80:20

Flocculant = PEO Molecular Weight 900,000

Flocculant Dosage, kg/t	Grade, % Apatite	Recovery, %
0.5	82.3	97.4
0.5	84.3, 83.9	96.3,95.7
2.0	85.0	95.3

CHAPTER 7
ADSORPTION MECHANISM OF POLY(ETHYLENE OXIDE)

Introduction

Adsorption mechanisms of polyethylene oxide (PEO) on solid surface have been extensively studied. However, most of the past studies [Rub76, Che85] have been directed towards understanding the adsorption behavior of lower molecular weight PEO (less than 1 million), on well characterized precipitated or pure silica. The ease in modifying silica surface charge by simple heat treatment or changing the pH helped in understanding the polymer-solid interactions. The isolated silanols and the siloxanes or methylated sites on the silica surface have been identified as the principal adsorption sites for PEO molecules. The adsorption mechanism on the former sites is believed to be hydrogen bonding and on the latter hydrophobic interactions. In some cases, both these mechanisms may be possible [Rub76]. It is reported that PEO adsorption is not favored, if the regions between the sites were hydrated or ionized.

Two other mechanisms are possible for the adsorption of PEO on solid surfaces.

(i) Slight anionicity of the PEO molecule can result in electrostatic interactions, especially if the particles are positively charged.

(ii) Complex binding of PEO with ions such as K^+, Cd^{2+}, Mg^{2+}, etc., [Bai59, Bai76, Kje81, Ana87] could facilitate adsorption, if these are present as adsorbed species on the solid surface.

In this chapter adsorption mechanisms of PEO on apatite and dolomite are studied. By combining the knowledge of flocculation, adsorption coupled with FTIR and heat of adsorption studies the principal adsorption sites are identified.

Identification of Sites on the Apatite and Dolomite Surface

Surface Analysis

FTIR spectra of apatite and dolomite are shown in Figure 4.6. The major peaks are identified according to Ince et al. [Inc91] and Farmer [Far74]. The peak at 1055 cm^{-1} in both samples indicates the presence of clay type of impurity (part of the acid insoluble in the chemical analysis). The dolomite sample has an isolated hydroxyl group at 3621 cm^{-1}, whereas in apatite there is bonded hydroxyl group at 3400 cm^{-1}. Previously, the isolated groups have been shown to act as specific chemical groups. The broad band of water, on the other hand may interact physically or chemically. Earlier studies on silica-PEO [Rub76, Che85] and silica-polyacrylic acid (PAA) [Tad78] have shown direct correlation between the presence of the isolated -OH groups on the surface and the saturation adsorption of the polymer molecules capable of hydrogen bonding. The different nature of the hydroxyl groups present on apatite and dolomite was further confirmed by the weight loss from DTA/TGA analysis. A sudden decrease in the weight was observed in dolomite sample at about 700 ^{o}C due to decomposition of the carbonates to oxides and only a slight decrease in the weight was observed in the apatite sample, possibly due to loss of water.

Direct observation of the mechanism for PEO adsorption on dolomite and apatite may be obtained by comparing the IR spectra of the powders with and without the polymer adsorbed onto it. This method of comparing spectras has been employed in previous studies to understand the polymer-solid interactions in a number of systems [How67a, How67b, Far74, Inc91, Pra91b]. No difference in the spectra of dolomite and apatite with or without PEO adsorbed was observed in the present case. Although a slight shift in the isolated hydroxyl group peak, as was observed by Howard and McConnel [How67b] and Fripat and Uytterhoeven [Fri62] for adsorption of PEO in a non-aqueous system was expected as a direct evidence of hydrogen bonding, however, this was not observed in the present aqueous system, possibly due to the insensitivity of the IR to the formation of hydrogen bonding.

The effect of physically adsorbed water or isolated hydroxyl groups on adsorption, may be evaluated by estimating the relative number of hydroxyl groups on the solid surfaces. At present there are no methods available for estimating the number of isolated and bonded -OH groups on the apatite and dolomite surfaces. Ignition [Che85] method has been suggested to estimate total number of -OH groups on silica surface by measuring the loss in weight by heating from 115^{0}C to 1150^{0}C, which for apatite and dolomite can not be used because of chemical decomposition of the solids at relatively low temperatures. Titration with certain chemicals, capable of interacting with isolated hydroxyl groups (such as tetra ethyl ortho silicate) may be done to estimate these groups, but due to the soluble nature of apatite and dolomite, this method also cannot be used [Yos92]. An attempt was made to understand the role of the isolated -OH groups by diffuse reflectance FTIR spectroscopy.

Dolomite samples used in this study have exhibited varying adsorption and flocculation behaviors. A direct correlation between saturation adsorption, flocculation and presence of isolated -OH groups is evident from the data presented in Table 7.1.

Table 7.1: Correlation Between The Adsorption, Flocculation And The Intensity Of The Isolated -OH Groups On The Surface.

Mineral	Adsorption, mg/m^2	Amount Flocculated *, %	Intensity of the Isolated -OH peak
Apatite	0.43	0.0	absent
Dolomite A	2.18	98.5	very prominent
Dolomite B	1.93	92.1	prominent
Dolomite C	1.16	63.2	significant
Dolomite D	1.19	72.4	significant
Dolomite E	0.88	0.0	absent
Dolomite F	0.31	0.0	absent

* Flocculant Dosage 1 kg/t

Comparison of the flocculating and non-flocculating dolomite spectras will, therefore, help in identifying the surface groups capable of interacting with PEO. IR spectra of the different dolomite samples are shown in Figures 7.1-7.3. It can be seen that the dolomite samples with isolated hydroxyl groups (sample A,B,C and D) have a significantly higher adsorption density of PEO as compared to the samples without this peak (sample E and F). A direct correlation seems to exists between samples with isolated -OH groups and their ability to flocculate with PEO of 5 million molecular weight. It should be noted that dolomite samples exhibiting flocculation contain apatite impurities besides the isolated -OH groups. These clearly could not be the binding site for PEO adsorption as pure apatite did not flocculate with this polymer. The above data would further rule out the possibility that the adsorption on dolomite takes place because of the interaction of PEO with Mg^{2+} or any other ionic species on the surface of dolomite. The varying flocculation behavior of dolomite samples, would also rule out the possibility of the interaction of sodium silicate (dispersant used in the study) with PEO to be a major cause for flocculation of dolomite sample A.

Considering that the isolated hydroxyl groups act as the principal adsorption sites for PEO, a change in the density of these sites is expected to influence the flocculation behavior of the material. As mentioned earlier, the nature of the surface group and the surface charge can be altered by changing the pH or heating the solids to various temperatures. The effect of these pre-treatments on dolomite sample A and apatite are discussed next.

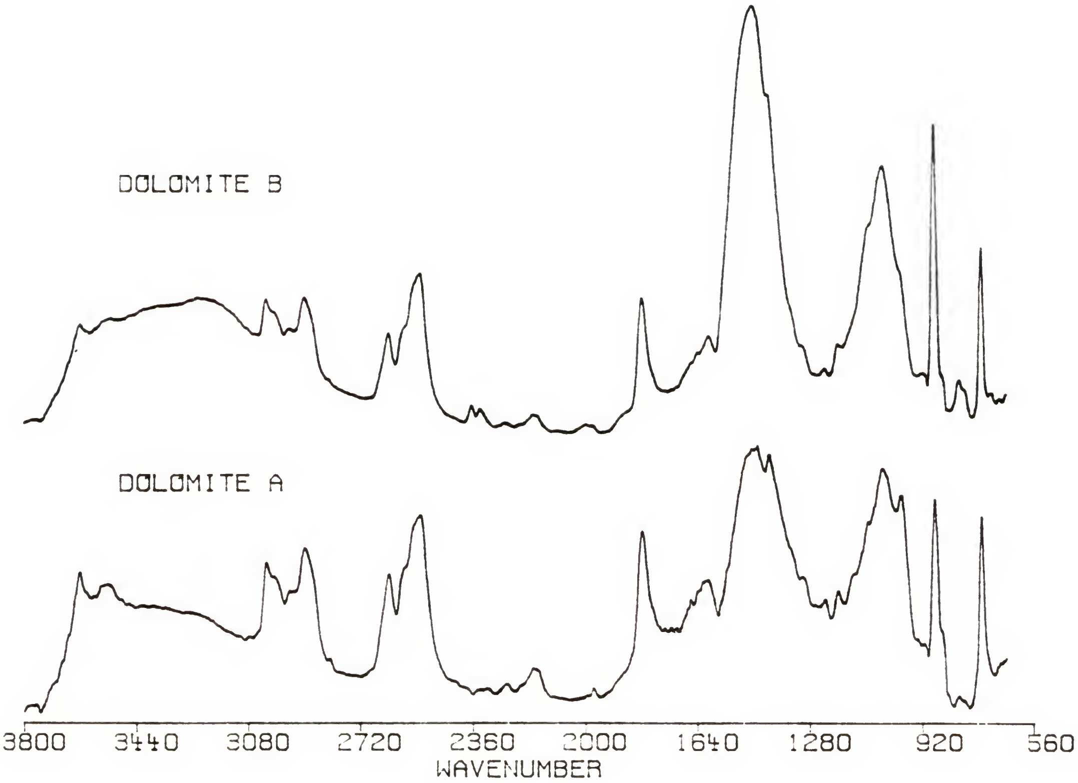


Figure 7.1: Diffuse Reflectance Spectra Of Dolomite Samples (A and B).

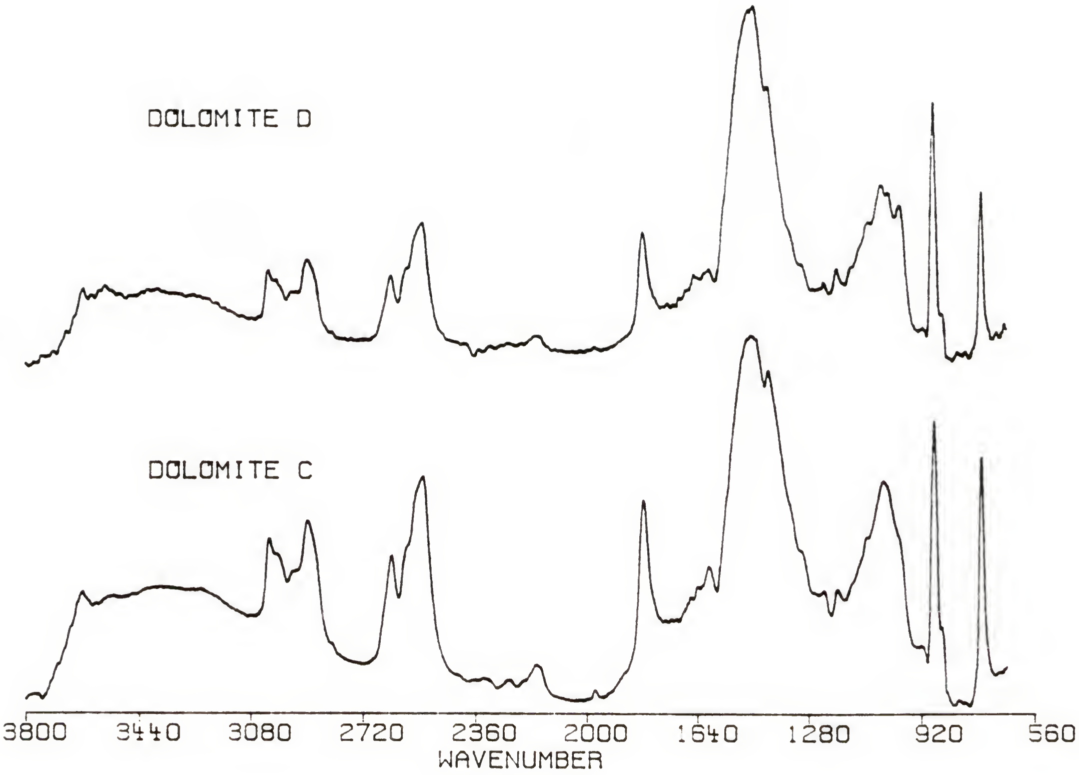


Figure 7.2: Diffuse Reflectance Spectra Of Dolomite Samples (C and D)

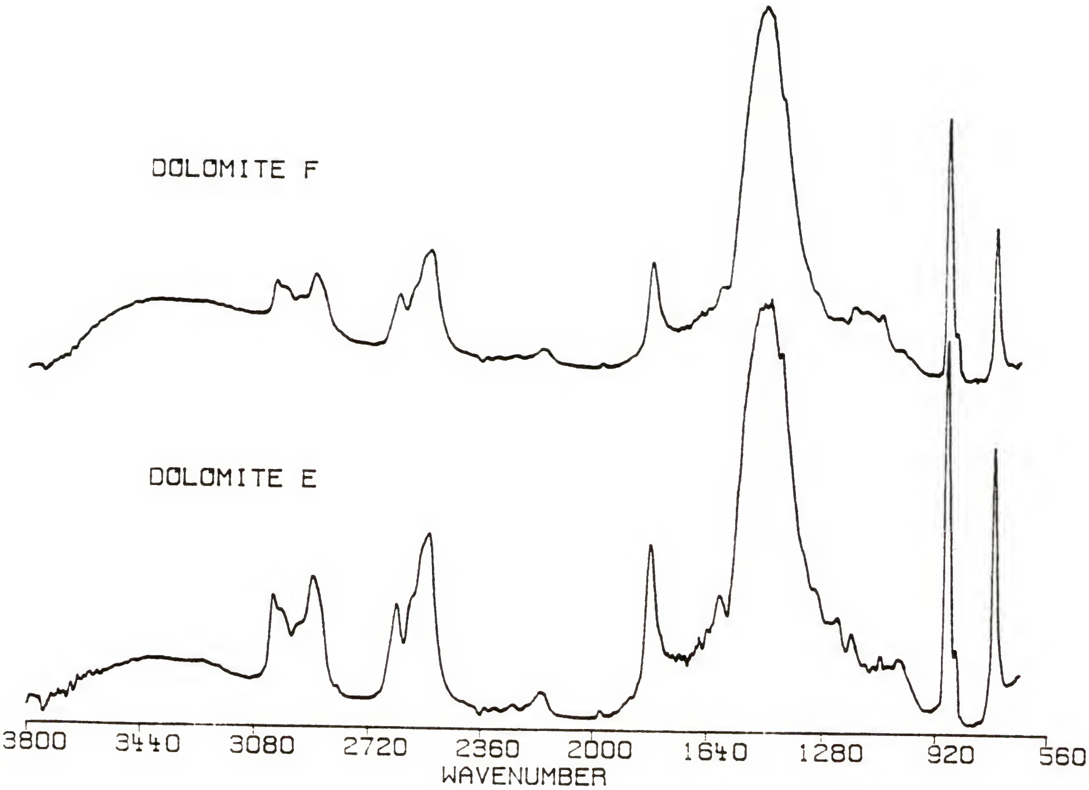


Figure 7.3: Diffuse Reflectance Spectra Of Dolomite Samples (E and F).

Effect Of pH Treatment

It is well known that both apatite and dolomite surfaces have a significant dissolution at low pH. Also, a change in pH would result in varying surface charge (zeta potential) characteristics.

pH treatment to change surface groups

IR spectra of the dolomite sample A treated at different pH values are shown in Figure 7.4. The intensity of the peak at 3621 cm^{-1} (isolated hydroxyl group) reduces drastically as pH decreases and at an extreme low pH value of 1.5, this peak is completely eliminated.

After pH treatment the material was first washed free of the dissolved ions and subsequently flocculated at pH 9.5. As seen from Figure 7.5, no floc formation was observed with samples pre-treated at pH 1.5, indicating that the isolated -OH groups are essential for PEO adsorption and floc formation.

The above observations may be explained also by the acid-base reaction theory between the dolomite sample A and PEO. The dolomitic surface is basic [Pug92] due to the presence of isolated -OH groups thereby facilitating adsorption of PEO, a lewis acid [Bro89].

No significant difference in the surface groups of apatite (or in its flocculation behavior with PEO) was observed by treating the samples at different pH values as expected (see Figure 7.6).

pH treatment to change surface charge

The zeta potential behavior of dolomite samples is plotted in Figure 7.7. It can be seen that samples E and F show double IEP which is in agreement with earlier studies [Cha86, Inc87]. The second IEP in dolomite is believed to be due to precipitation of

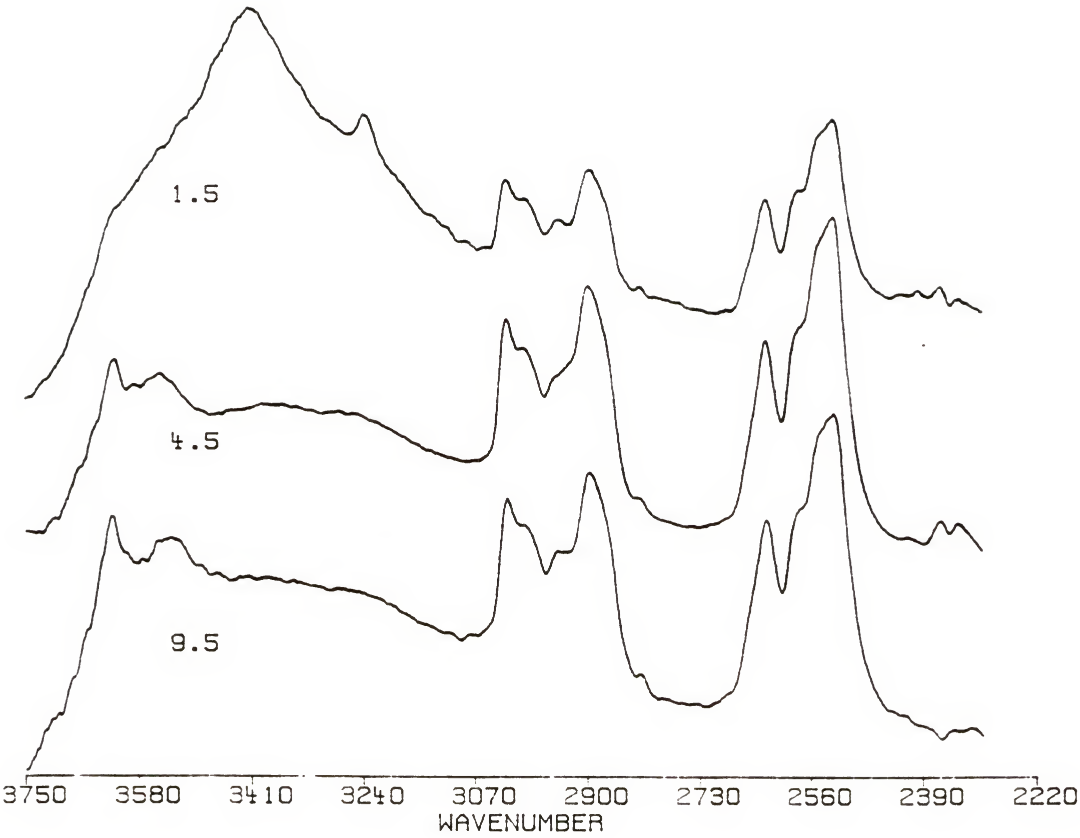


Figure 7.4: Effect Of pH Treatment On Dolomite

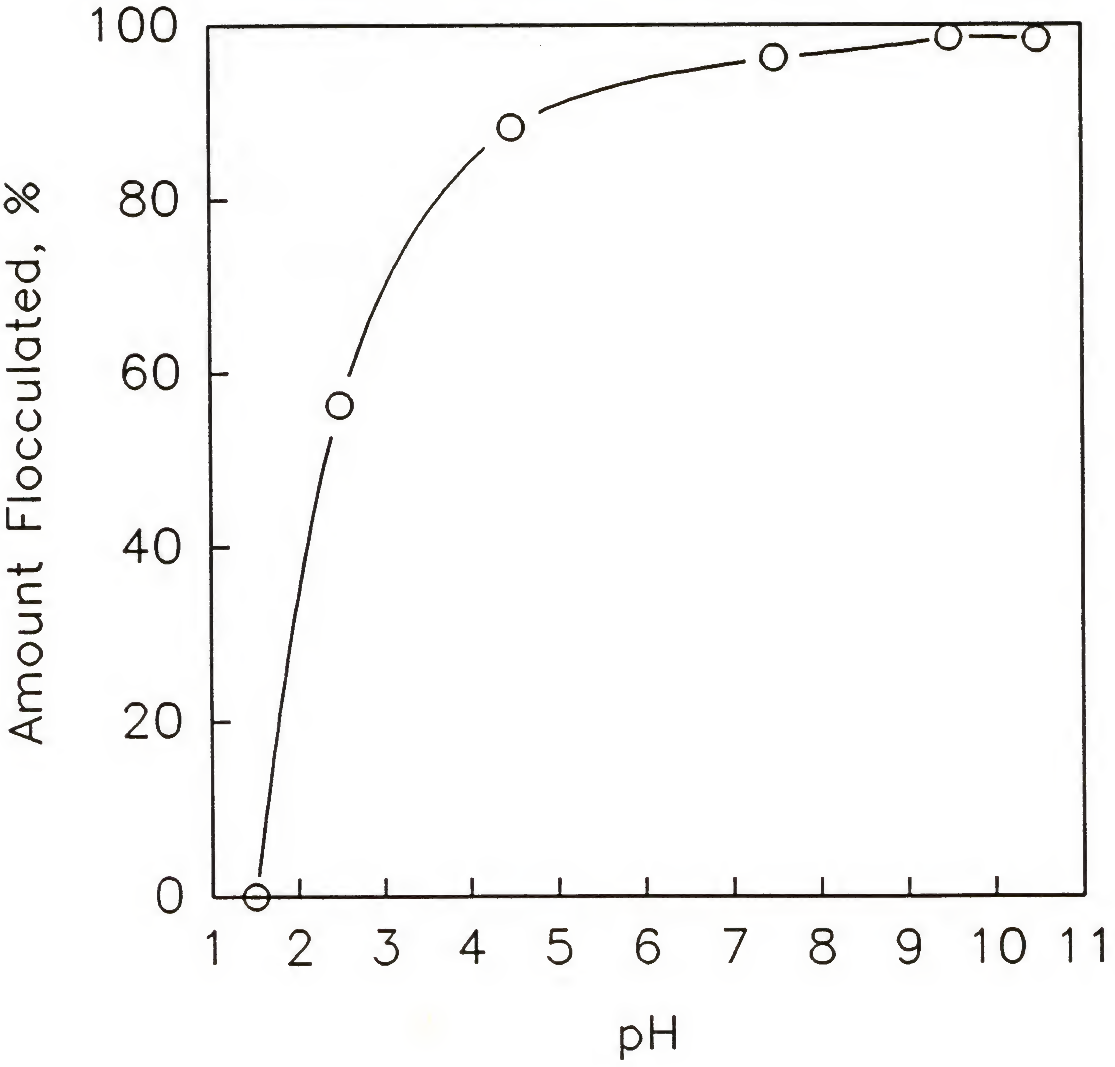


Figure 7.5: Effect Of pH Treatment On The Amount Of Flocculation Of Dolomite.

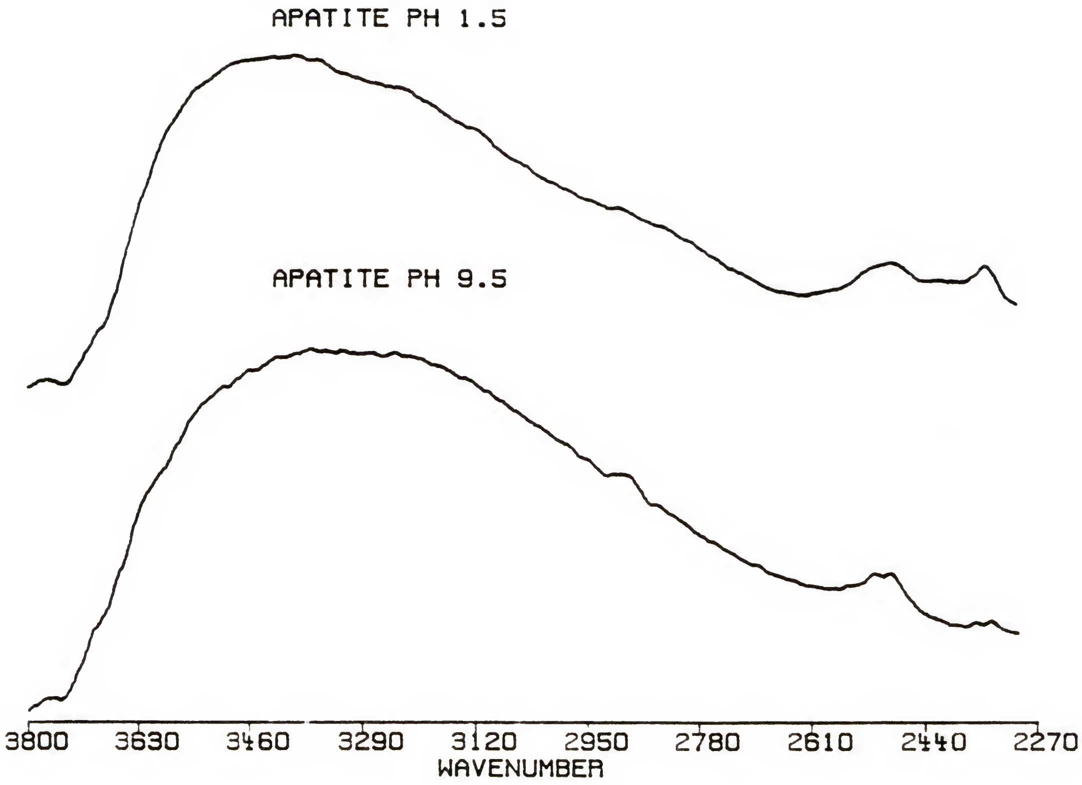


Figure 7.6: Effect Of pH Treatment On Apatite.

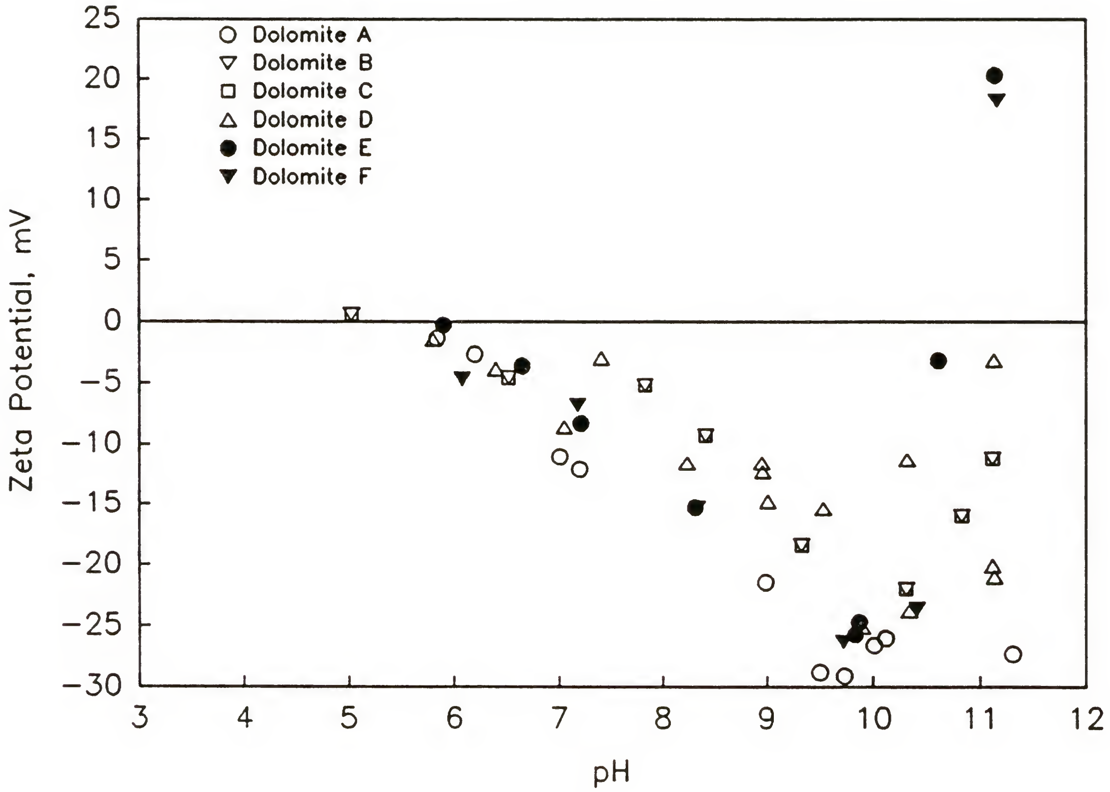


Figure 7.7: Zeta Potential Behavior Of Various Dolomite Samples.

magnesium hydroxide on the surface. It is interesting that the dolomite samples exhibiting double IEP (sample E and F) do not have isolated -OH groups on the surface. It is known that the magnitude of the zeta potential depends strongly on the ionic strength of the medium. Further, dolomite is known to have significant dissolution, therefore, it is important to ascertain the effect of ionic strength on the zeta potential and on flocculation. It is clear from Figure 7.8 that dissolution of the dolomite samples differs from one another. Dolomite sample A particles with higher surface area was expected to dissolve more but the opposite was observed. Infact the samples E and F with the smallest surface area, yielded maximum dissolution. The high ionic concentration of the suspensions in these cases should force the PEO molecule to "salt out" on the solid surface and aid in adsorption [Rub76]. However, at a higher ionic strength the polymer is also expected to be "more" coiled, thereby adversely affecting floc formation [Che85]. It is interesting that the zeta potential of these samples is similar. Rubio and Kitchner showed that flocculation with PEO is enhanced by the addition of salt in the silica suspension but these studies were performed at very low ionic concentrations, unlike those encountered in the dissolution of dolomite and apatite. Flocculation of sample A in the supernatant of dolomite E and vice versa did not change the aggregation behavior. Since ionic concentration was not observed to influence flocculation in the present studies, the isolated groups can be considered to be the primary sites on the surface interacting with the PEO molecules.

It should be noted that the samples having higher dissolutions exhibit the double IEP and do not exhibit flocculation. At present it is difficult to explain the observation of double IEP, absence of the isolated hydroxyl groups and higher dissolutions. The reasons for dolomite having isolated hydroxyl groups on some samples and being absent

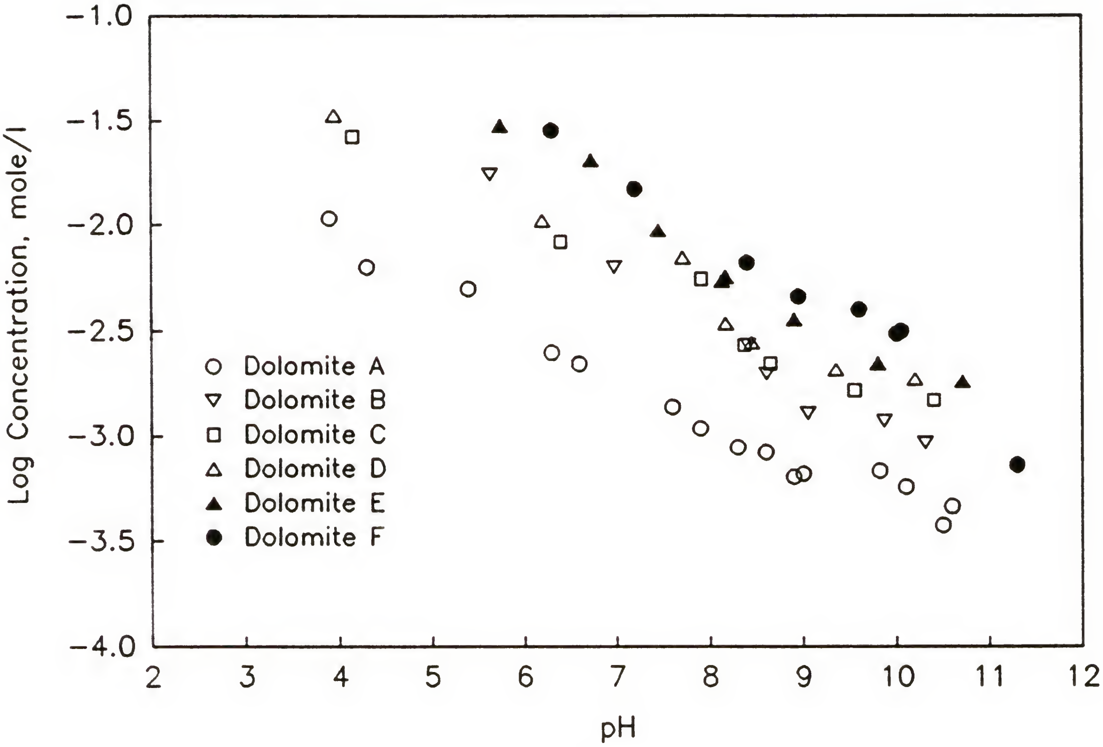


Figure 7.8: Dissolution Behavior Of Various Dolomite Samples.

on the others also are also not well understood.

Effect Of Temperature Treatment

Isolated -OH groups on the surface are known to concentrate at higher temperatures [Che85]. A number of studies have been conducted in the past to elucidate the mechanisms of the change in density of the isolated hydroxyl groups on silica and alumina surfaces [Kis72]. The number of -OH groups present on the silica surface under different conditions were complied by Snoeynik [Sno72] and were reported to decrease with increase in temperature.

It can be seen from Figure 7.9 that on pretreating the dolomite sample A at a higher temperature, the isolated -OH groups become more prominent but the total flocculation remains unchanged (See Figure 7.10). Although treatment above 700°C decomposes the sample, an increase in the isolated -OH peak was observed and no change in flocculation occurred.

As expected, increasing the temperature of apatite to 650 °C revealed the presence of isolated -OH groups (see Figure 7.11), however, no flocculation was observed, indicating the requirement of a critical adsorption density (or critical number of sites for adsorption on the surface), for floc formation. In other words the surface should not be totally dehydrated upon heating. Flocculation of a mixture of apatite and dolomite pre-treated at 700°C, resulted in a slight increase in selectivity as compared to the mixture of untreated samples where a complete loss of selectivity occurred, indicating that the apatite surface is significantly affected by heat treatment.

The present results show that adsorption of PEO is higher on dolomite samples with isolated hydroxyl groups. A possible explanation is that the isolated -OH groups

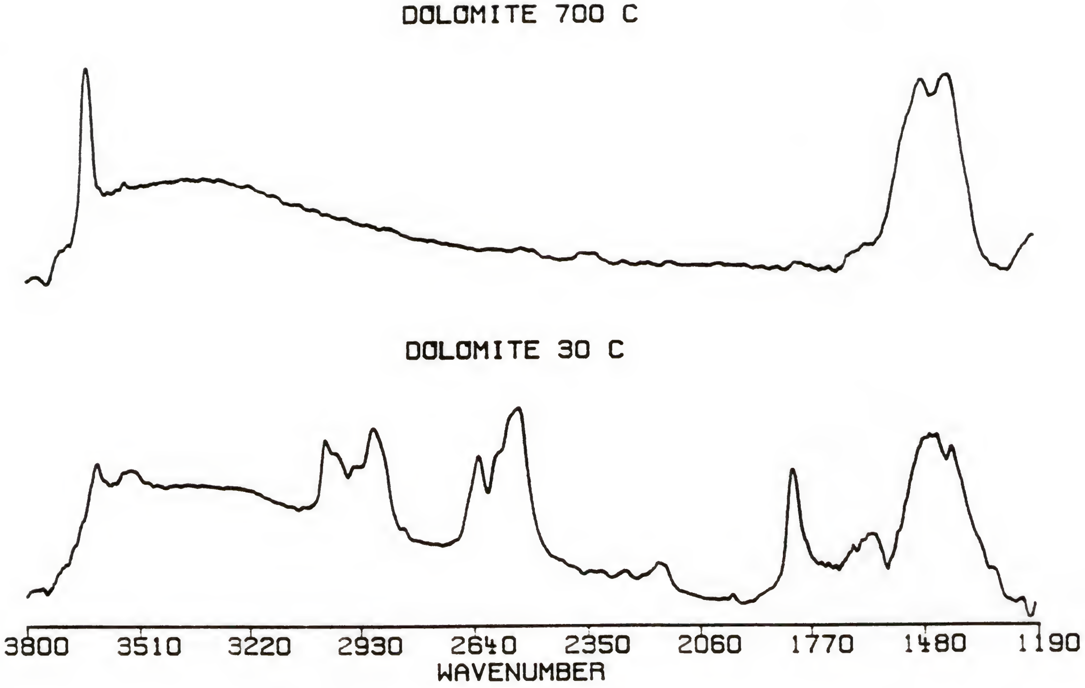


Figure 7.9: Effect Of Temperature Treatment On Dolomite Surface.

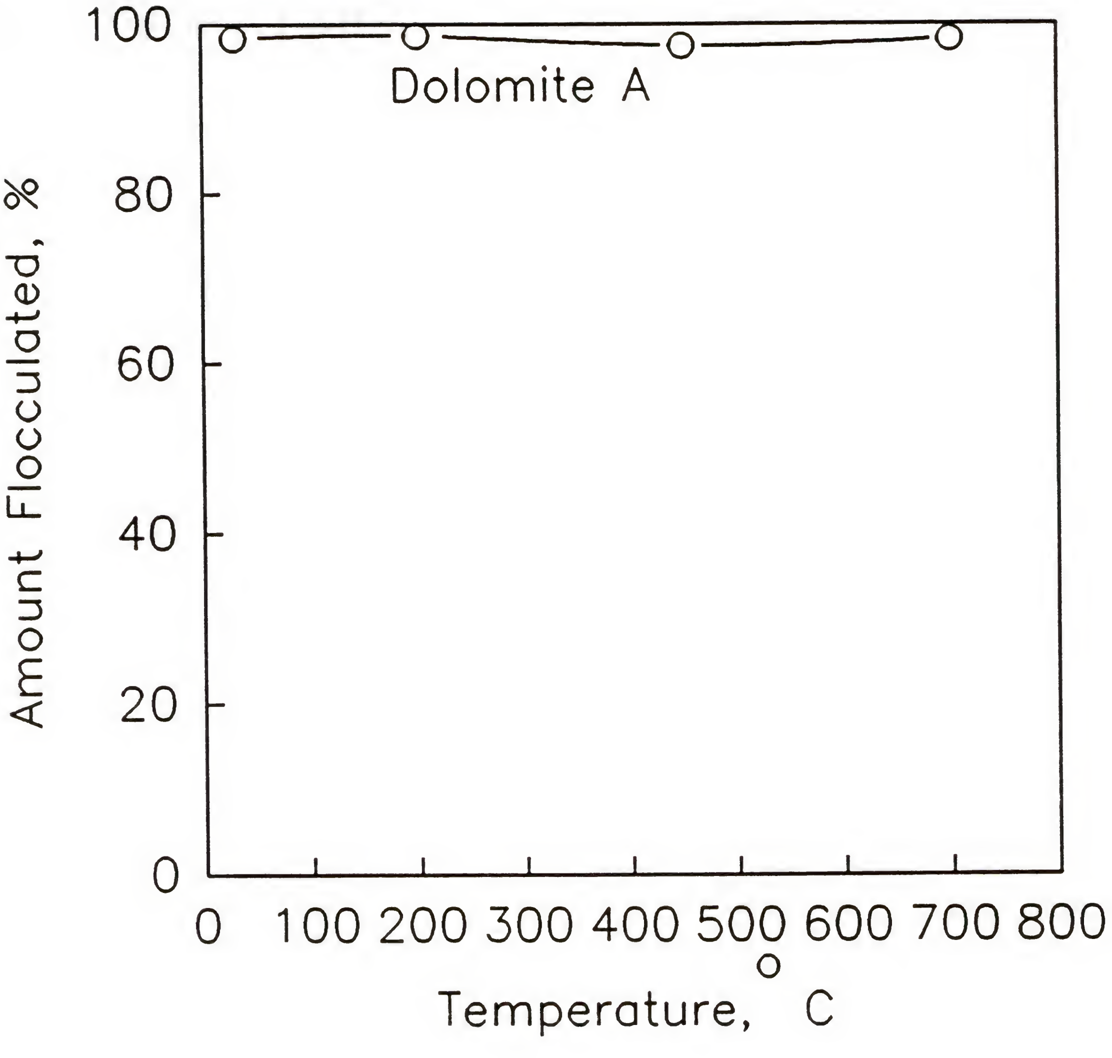


Figure 7.10: Effect Of Pre-Treatment Temperature On Flocculation Of Dolomite.

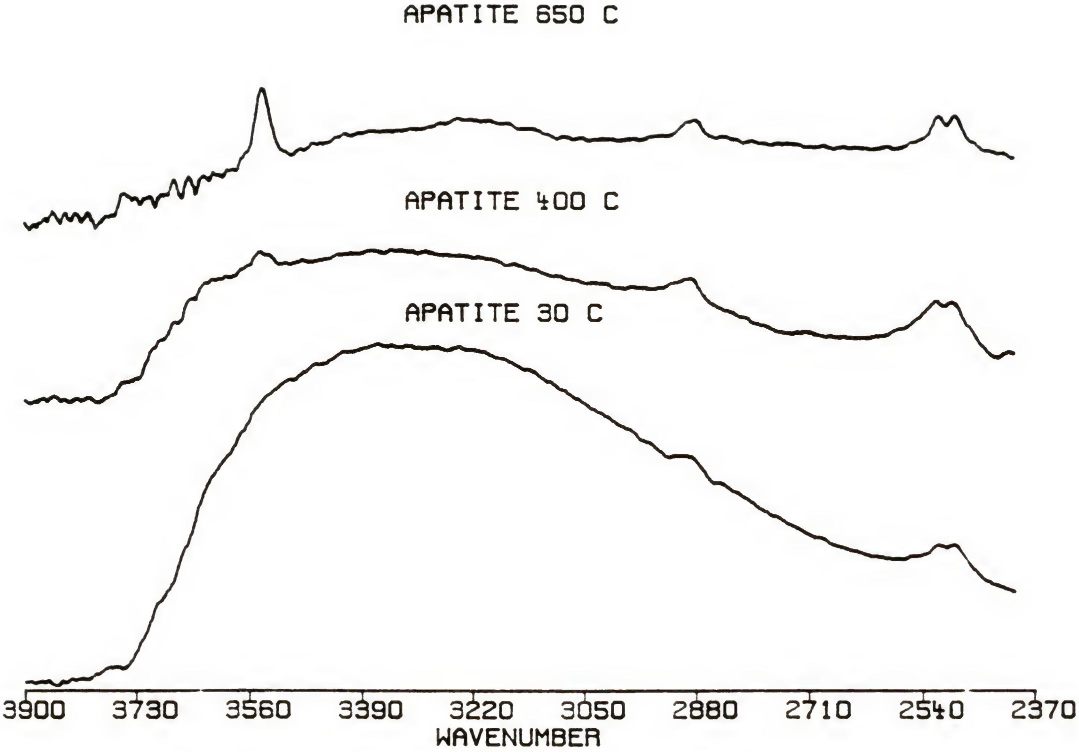


Figure 7.11 Effect of Temperature Treatment on Apatite.

provide the best adsorption sites, acting as proton donor in hydrogen bonding to ether oxygen. The binding may be schematically represented as:

$$-CaOH......O(CH_2CH_2)=$$

$$-MgOH......O(CH_2CH_2)=$$

This hypothesis was previously suggested for adsorption of polyacrylamides [Fon63] and for low molecular weight on PEO by Howard and McConnel [How67a, How67b] and for copolymer of ethylene oxide and methyl methacrylate on silica [Fon63]. Complete dehydroxylation would render the surface incapable of providing the proton, consequently the adsorption would be absent as was observed experimentally. On the other hand the adsorption on apatite may occur as follows

$$-[APATITE].H_2O...O(CH_2CH_2)=$$

It can be concluded that the principal adsorption sites of PEO on apatite and dolomite are physically adsorbed water and isolated -OH groups respectively. Additionally, heat of adsorption of PEO on apatite and dolomite were found to be of similar order, thereby implying that adsorption mechanism on apatite and dolomite were thermodynamically similar in nature.

Thermodynamic Parameters Of Adsorption - Heat Of Adsorption

Adsorption characteristics of the polymers can be expressed by thermodynamic parameters such as ΔG (Gibbs free energy change for adsorption), ΔH (enthalpy change during adsorption), and ΔS (entropy change for the process). Evaluation of these parameters can give valuable insight into the possible interactions/mechanisms underlying the polymer adsorption process. A negative value of ΔG is required for the adsorption to take place. Enthalpic changes (ΔH) gives an indication of the bond strength. The higher the value of the heat of adsorption, the weaker is the bond between the adsorbate and the substrate. Since adsorption of the polymer molecules onto solids from dilute solution is believed to be entropically driven, the sign of ΔS would indicate the direction of adsorption (ΔS positive) or desorption (ΔS negative).

Attempts have been made in the past to estimate the values of the thermodynamic parameters [Kor58, Kil76, Pra80, Coh82, Att91]. It should be noted that techniques are not available to determine ΔG and ΔS directly; however, ΔH can be experimentally measured. The ΔG value is generally estimated from the equilibrium adsorption data with the assumption that the adsorption of a long chain organic molecule is reversible and that an equilibrium is established in the system. The other parameters (ΔH and ΔS) are estimated by determining the adsorption isotherms at different temperatures assuming them to be independent of temperature. In the case of adsorption of polymer molecules, unlike other smaller molecules, these assumptions may not be valid since the adsorption mechanisms are complex, and more than one type of adsorption force may be acting at any instant.

There is limited information in the literature for direct measurements of ΔH. Most of the reported work [Fow84, Bot88, Den90] has been concerned with determination of the polymer conformation on the polymer surface and estimation of the fraction of the bonded polymer segments. Bottero et al. [Bot88] have attempted to interpret the heat of adsorption results to elucidate mechanisms of polyacrylamide adsorption on sodium montmorillonite. Also, Fowkes and co-workers [Fow84] measured the heat of adsorption of a polymer onto solid surface in a non-aqueous medium using a flow cell type calorimeter. All of these studies have reported negative values of ΔH, indicating that the enthalpy part of the free energy aids in increasing the driving force for adsorption. The heat evolved have been of the order of 1-10 kJ/mole of the monomer.

The surface hydroxyl groups have been identified by FT-IR studies, as the principle adsorption sites for PEO/PEG on apatite and dolomite substrates and the major binding mechanism is expected to be hydrogen bonding. In this study heat of adsorption of PEO/PEG on apatite and dolomite are used to evaluate the nature of interaction between the polymer molecule and the solid surface.

In the present study, since hydrogen bonding is expected as the main adsorption mechanism, the heat of adsorption values are expected to be similar. The heat of wetting indicated that the interaction of dolomite and apatite surfaces with water is similar (See Table 7.2). The adsorption of PEO on apatite exhibited an exothermic value while in dolomite samples this was true only for the lower molecular weight polymer. In the case of 5 million molecular weight PEO, a high endothermic value was measured. This implies that the higher molecular weight PEO is enthalpically not favored to adsorb on the dolomite surface. A similar endothermic value for adsorption of 5 million PEO on dolomite (different sample), alumina and silica was reported by Moudgil et al. [Mou92]. Although endothermic values may be explained in terms of the exothermic heat of dissolution of PEO and hydration water molecules associated with the ether oxygen, the values reported for other polymer solid systems in the literature [Kor58, Kil76, Coh82, Bot88, Den90] are significantly lower and generally exothermic.

Heat of adsorption experiments were conducted at a low dosage (0.2 kg/t). At this dosage no residual concentration is expected and this can be inferred from the adsorption isotherms (See Figure 4.10).

Table 7.2: Heat Of Adsorption Of PEO On Apatite And Dolomite.

Heat of Wetting : Dolomite = -138 cal/mole

: Apatite = -198 cal/mole

Polymer Molecular Weight	Heat of Adsorption, Kcal/mole of PEO monomer	
	Apatite	Dolomite
3400	-8.89, -7.51	-3.23, -2.78
5×10^6	-6.75, -5.46	7.42, 8.76, 7.80

It is well known that apatite and dolomite have significant dissolution in water, especially at low pH and various ionic species exist in the solution depending on the pH of the solution. At the experimental pH of 9.5 there is limited dissolution of these minerals, though dolomite has a significantly higher dissolution as compared to apatite (see Figure 4.1). PEO has been reported to form bi-phase in salt solution (or in high ionic concentration solutions) [Bai59, Ana87]. Further the tendency to form bi-phase increases with increase in salt or polymer concentration, molecular weight of the polymer and the ionic charge associated with the cation and the anion of the salt. The bi-phase formation is typically observed at reasonably high concentrations as compared to those encountered in this study. However, it is believed that the segregation of the salt and the polymer takes place on the molecular level even at extremely low concentrations [Ana87]. Therefore, the heat effects of polymer dilution in DI water and the supernatant of the minerals may be expected to be vastly different due to the interactions of the macromolecules with dissolved salts.

To understand the contribution of the dissolved ion interaction with the polymer molecules, dilution of PEO in the supernatant of apatite and dolomite was attempted. An endothermic heat of dilution was measured (Table 7.3). Further, the higher endothermic value is reported for 5 million molecular weight polymer as compared to the lower molecular weight PEG. It is to be noted that a endothermic heat of dilution of PEO in water is measured , which is in agreement with earlier studies by Killman et al. [Kil76]. Highly endothermic heat values are observed for PEO dilution in dolomite supernatant, possibly due to larger dissolution as compared to that in apatite supernatant.

Table 7.3: Heat Of Dilution Of PEO In Apatite And Dolomite Supernatant.

Polymer Molecular Weight	Heat of Dilution kcal/mole of PEO Monomer		
	Water	Apatite Supernatant	Dolomite Supernatant
3400	0.44, 0.40	1.73, 2.27	4.32, 4.24
5×10^6	0.57, 0.53	3.27, 3.53	11.34, 11.16

Accounting for the contribution of the dilution of the PEO molecule, the heat of adsorption on both apatite and dolomite are of similar order indicating similar bonding (See Table 7.4) of the polymer onto the surface. It can be inferred from the data in Table 7.4 that the adsorption of PEO on apatite is by a flatter conformation as the heat of interaction is independent of the molecular weight [Den90]. On the other hand due to the smaller ΔH value for higher molecular weight PEO adsorption on dolomite, a more open conformation is expected [Den90]. This is in agreement with the earlier information for PEO adsorption on apatite and dolomite, where the amount of polymer adsorbed on apatite scales as $M^{0.07}$ as compared to $M^{0.12}$ on dolomite, indicating a flatter conformation on the apatite surface.

Table 7.4: Corrected Heat of Adsorption of PEO on Apatite and Dolomite Surface.

Polymer Molecular Weight	$\Delta H_{measured}$, kcal/mole of PEO monomer		$\Delta H_{dilution}$, kcal/mole of PEO monomer		$\Delta H_{interaction}$, kcal/mole of PEO monomer	
	Apatite	Dolomite	Apatite	Dolomite	Apatite	Dolomite
3400	-8.20	-3.00	2.00	3.40	-10.20	-6.40
5×10^6	-6.10	8.00	4.3	11.30	-10.40	-3.30

CHAPTER 8
CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Summary

Separation of dolomite and apatite using polyethylene oxide as a flocculant was attempted by selective flocculation process. An effective dispersion of apatite and dolomite in water, a pre-requisite for selective flocculation process, was achieved with the aid of sodium silicate dispersant.

Single mineral tests indicated that polyethylene oxide (molecular weight 5 million) flocculates dolomite but not apatite. However, mixed mineral tests did not exhibit the expected selectivity. Further investigation revealed that the major reason for the loss in selectivity was heteroflocculation. Heteroflocculation was controlled by using a site blocking agent (SBA). It has been demonstrated that the lower molecular weight fraction of the flocculant itself can be an effective SBA. The most efficient SBA is the highest molecular weight fraction of the flocculant which is not capable of flocculation. This has been demonstrated both experimentally and mathematically. The improved selectivity is attributed to a significant decrease in the adsorption of the flocculant on apatite in the presence of the SBA. The non-equilibrium and the equilibrium adsorption isotherms of the SBA on apatite and dolomite particles indicated that contact time (conditioning time) is not an important process parameter.

A simple quantitative model has been proposed to describe the site blocking concept. It has been demonstrated that in the presence of the site blocking parameter the collision efficiency factor decreases both for single and mixed mineral systems. The optimum in single mineral flocculation takes place typically at a dosage corresponding to less than half the surface coverage. Also, it is not possible to depress the flocculation of an active component. The depression in flocculation in mixed mineral system is directly related to the site blocking parameter ($\bar{\Phi}\bar{\theta}$). The molecular weight of the SBA (related to $\bar{\Phi}$) was found to be a more important parameter for blocking sites for flocculant adsorption as compared to the SBA dosage.

The choice of equivalent active sites helps in explaining the flocculation phenomena without considering the polymer conformation or the number of adsorption sites. It is seen that flocculation is observed in a system with equivalent Φ greater than about 0.4. The reasons for this critical value of Φ at the present moment are not very well understood, although it seems to be related to the interaction energy of the polymer with the surface for optimum bridging. This concept can be used to identify conditions for achieving selectivity during the selective flocculation process. Selective floc formation may be expected if the effective Φ for the system is below 0.4, which seems to be an important criteria in controlling heteroflocculation, a major reason for the loss of selectivity.

It was also determined that although apatite and dolomite particles were porous, but for the range of molecular weight of PEO studied they behaved as compact entities. Further, it has been demonstrated that PEO adsorption on apatite and dolomite is of random coil conformation. Also, on increasing the molecular weight of PEO the saturation adsorption reaches a plateau at 5 million molecular weight implying that the entire surface consists of active sites.

Adsorption of PEO on apatite is attributed to hydrogen bonding of the polymer molecule with surface water. On the other hand, flocculation of dolomite samples with PEO is primarily due to the adsorption of the polymer on the isolated hydroxyl groups present on the surface. PEO adsorption on dolomite may also be due to Lewis acid-base reaction of the ether oxygen with isolated -OH groups on the dolomite surface. The change in the intensity of the isolated-OH groups by either pH treatment or heating was determined to alter the flocculation behavior. Presence of isolated hydroxyl groups was determined to have a major influence on flocculation of different dolomite samples with PEO, inspite of their similar chemical and crystal structure.

An exothermic heat was observed for the adsorption of lower molecular weight PEO on dolomite and apatite surfaces. However, for high molecular weight PEO (5 million) the heat of adsorption on apatite remains exothermic, while that for dolomite it is endothermic. This has been explained in terms of dilution of the polymers in the supernatant of these solids. PEO interactions with salt solutions have been shown to be highly endothermic, therefore, PEO is expected to form a bi-phase with a stronger driving force, as the "salting out" phenomena in this case is enthalpically and entropically favorable. The heat of interaction of PEO molecules on apatite and dolomite surfaces was found to be of similar nature. The adsorption of PEO/PEG on apatite was found to be flatter as compared to dolomite.

Suggestions For Future Work

Further studies need to be undertaken to understand the universality of this process. It has been found that different dolomite have varying flocculation behavior with PEO, therefore, a generic flocculant for this material needs to be developed. It possibly should take advantage of the specific interaction with the magnesium ion present only on the dolomite surface. Further attempts should be made to study the effect of wet and dry grinding of the mixtures on selectivity. Grinding the mixtures together can have significant effects on the surfaces of the particles, e.g., forming a thin coating of one mineral on the other, thereby altering the adsorption and flocculation behavior. This step is important for economic viability of this process.

Floc characteristics are known to affect the separation in selective flocculation process. For example, large and dense flocs can be separated by sedimentation, however, floc flotation may be required for small and fluffy flocs. The effect of site blocking agents on the floc characteristics need to be studied in details for successful implementation of the process on an industrial scale.

In this study methods to generate or remove the isolated hydroxyl groups have been discussed. However, the control on such groups was not selective. Some work needs to be done to develop methods to selectively generate these groups on the desired surface. Also, generic methods to generate surface groups other than hydroxyl groups needs to be investigated.

The nature of the hydroxyl groups on the apatite and dolomite surface needs to be examined in detail. Developing correlations between the conformation of the adsorbed polymer with the nature of the hydroxyl groups on the surface would give valuable insight to developing selective flocculants. The nature of the hydroxyl groups can be studied by adsorbing probe molecules on this surface in both aqueous and non-aqueous phase. Interactions different from hydrogen bonding of PEO molecule with the surfaces of apatite and dolomite can be studied by Raman spectroscopy.

The mathematical model developed in this study to explain the site blocking concept and the abrupt start of flocculation at $\Phi = 0.4$, needs to be extended to study single mineral flocculation for solid-liquid separations. Also this concept to explain selectivity in mixed minerals needs to be studied in detail.

Due to unusual energetics of high molecular weight polyethylene oxide flocculation and adsorption of this polymer in strong salt solutions need to be studied. By changing the solvent power of the medium selectivity in flocculant adsorption may be achieved.

The site blocking concept should also be extended to systems with surfactants as Site Blocking Agent's.

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